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LONG TERM FATE AND PERSISTENCE OF STRANDED OIL AT CAPE HATT, N.W.T. AND FROM THE AMOCO CADIZ SPILL

EE-84

LONG TERM FATE AND PERSISTENCE OF STRANDED OIL AT CAPE HATT, N.W.T. AND FROM THE AMOCO CADIZ SPILL

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ABSTRACT

The site of the Baffin Island Oil Spill (BIOS) experiment on Cape Hatt N.W.T. was revisited in August 1985. The beach of Bay 11 and the countermeasure test plots in the "Z-lagoon" area were re-surveyed and sampled to ascertain the persistance and fate of the oil over the longer term. It is evident that the major changes took place following the initial stranding of the oil onto the shoreline of Bay 11 in 1981. The contaminating oils became more stabilized and in 1983 it was found that an asphalt pavement had formed in the upper intertidal zone of Bay 11. In the survey reported herein, there were no significant changes between 1983 and 1985 in the estimated volume of oil remaining on the Bay 11 beach or in the area of the beach sediments containing oil. The resilient asphalt pavement formations still remained. The backshore control plots in "Z-lagoon" showed that the volumes of total hydrocarbons are slowly decreasing by natural processes in this cold climate environment. The data that have evolved from this study to date can be used in lower latitudes (ice-free environments) and can be compared with data from real or experimental spills outside of the immediate study area.

The sub-tidal area adjacent to the oiled beach in Bay 11 was sampled along three transects perpendicular to the shoreline in order to determine the current extent and concentrations of hydrocarbon in the sediments. The concentrations did not appear to be changing markedly from those measured in 1983. It is supposed that both the input of new oil and the reduction of sedimented oil is very low at this time.

Asphalt pavement samples taken in 1985 from the site of the Amoco Cadiz were analysed by IR, gas chromatography and gas chromatography/ mass-spectrometry. The results indicate that the weathering processes had progressed much further in the oil spilled in a temperate climate (Amoco Cadiz) than they did in the Arctic (BIOS). This is attributed to both differences in ambient temperatures and the period of open water exposure. Compositional similarities between the asphalt-forming stranded oils in the two locations are not apparent.

RESUME

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Part 1: Cape Hatt Shoreline Study

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TABLE OF CONTENTS

Page

1.0 INTRODUCTION.....1-1

2.0 BIOS 1980 CONTROL PLOTS

2.1 Introduction.....2.1

2.2 1980 Backshore Control Plots.....2-2

2.3 1980 Low-Energy Intertidal Control Plots.....2-8

2.4 Summary.....2-12

3.0 BIOS 1981 COUNTERMEASURES EXPERIMENTS

3.1 Introduction.....3-1

3.2 Total Hydrocarbon Analysis Results.....3-2

3.3 Geochemical Analyses.....3-4

3.4 Summary.....3-5

4.0 BIOS 1982 COUNTERMEASURES EXPERIMENTS

4.1 Introduction.....4-1

4.2 Backshore Plots - Total Hydrocarbon Analysis Results....4-1

4.3 Backshore Plots - Geochemical Analysis Results.....4-12

4.4 Summary.....4-14

5.0 RAGGED CHANNEL EXPERIMENTS

5.1 Introduction.....5-1

5.2 Intertidal Hydrocarbon Analysis Results.....5-1

5.3 Intertidal Geochemical Analysis Results.....5-5

5.4 Surface Oil Cover Survey.....5-6

5.5 Estimated Oil Budgets.....5-13

5.6 Discussion.....5-15

5.7 Summary.....5-19

6.0 SUMMARY AND CONCLUSIONS

6.1 Z-Lagoon Sites.....6-1

6.2 Bay 11.....6-4

6.2.1 Surface Oil Cover.....6-4

6.2.2 Oil Budget Estimates.....6-6

6.3 Geochemical Data.....6-8

6.3.1 SHWR.....6-8

6.3.2 ALK/ISO.....6-11

6.3.3 AWR.....6-12

6.4 Conclusions.....6-13

7.0 REFERENCES.....7-1

APPENDIX A. Total Hydrocarbon

A1: Methods A-1
A2: Results A-3

APPENDIX B. Gas Chromatography

B1: Methods B-1
B2: Results B-4

1.0 INTRODUCTION

The primary objective of this study was to collect data as part of a continuation of the Baffin Island Oil Spill (BIOS) experiment that began at Cape Hatt in 1980. The field investigation involved resampling and resurveying of oiled control and countermeasure plots in the "Z-lagoon" area and the beaches of Bay 11 (Figure 1.1). This section of the report focuses on the field data and upon an interpretation of the total hydrocarbon and gas chromatography analyses. Details on the field sampling methods and on the analytical procedures are given in the appendices.

This report follows the same format as earlier BIOS Working Reports that were published in 1980, 1981, 1982, and 1983. For reference, Table 1.1 presents a list of the shoreline locations and the individual plots and the activities that were conducted at each site, as well as the codes used to designate each plot. A series of maps that identify the locations and the experimental sites is given in Figures 1.1, 1.2, and 2.1.

No data or information were collected during the summer of 1984, neither are any field studies associated with this programme planned for the summer of 1986. Although the interpretation of the geochemical data becomes more difficult with time, due to the many environmental factors that can affect the weathering of the hydrocarbons, there will continue to be an important information yield on the persistence and fate of the stranded oil in the Bay 11 area in

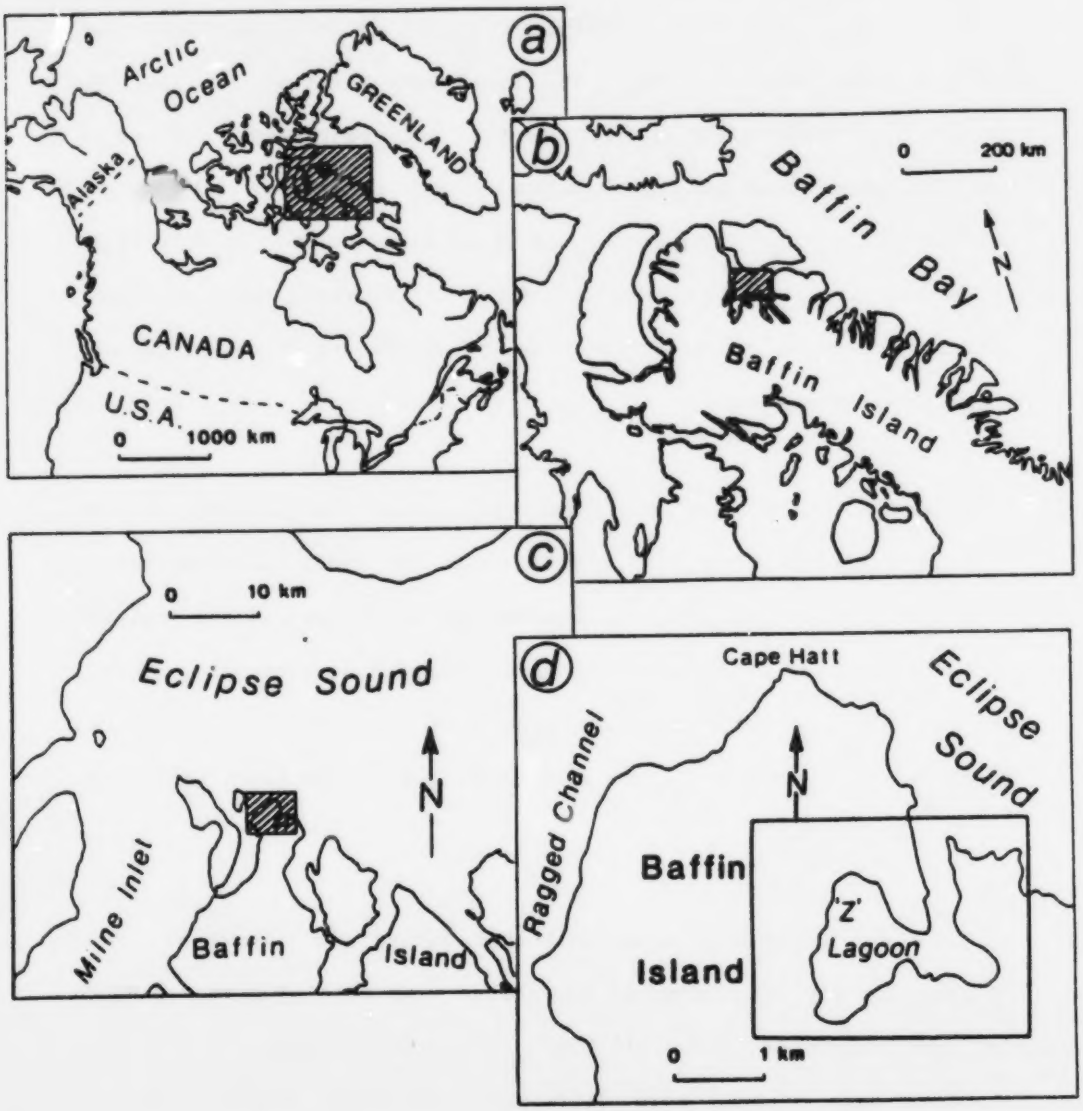


Figure 1.1 Regional location maps. The area within the rectangle in 'd' is given in more detail in Figure 2.1 (page 2-1).

Table 1.1 Shoreline Component Experimental and Control Plots.

Site	Location	Year Oil Spilled	Plot Designation	Type of Oil	Beach Zone	Activity
"H"	Bay 102	1980	H1	crude	intertidal	control
			H2	emulsion	intertidal	control
"L"	Bay 103	1980	L1	crude	intertidal	control
			L2	emulsion	intertidal	control
"C"	Crude Oil Point	1980	T1	crude	backshore	control
			T2	emulsion	backshore	control
"H"	Bay 102	1980	TE1	crude	backshore	control
			TE2	emulsion	backshore	control
"C"	Crude Oil Point	1981	CC	crude	intertidal	control
			CE	emulsion	intertidal	control
			D(B)C	crude	intertidal	dispersant (BP1100X)
			D(B)E	emulsion	intertidal	dispersant (BP1100X)
			D(E)C	crude	intertidal	dispersant (Corexit 7664)
			D(E)E	emulsion	intertidal	dispersant (Corexit 7664)
			MC	crude	intertidal	mixing
			ME	emulsion	intertidal	mixing
			SC	crude	intertidal	solidifier
			SE	emulsion	intertidal	solidifier
Ragged Channel	Bay 11	1981	-	crude	intertidal	control
"I"	Bay 106	1982	ICC	crude	intertidal	control
			ICE	emulsion	intertidal	control
			ID(B)C	crude	intertidal	dispersant (BP1100X)
			ID(B)E	emulsion	intertidal	dispersant (BP1100X)
			ID(E)C	crude	intertidal	dispersant (Corexit 7664)
			ID(E)E	emulsion	intertidal	dispersant (Corexit 7664)
			IMC	crude	backshore	mixing
			IME	emulsion	backshore	mixing

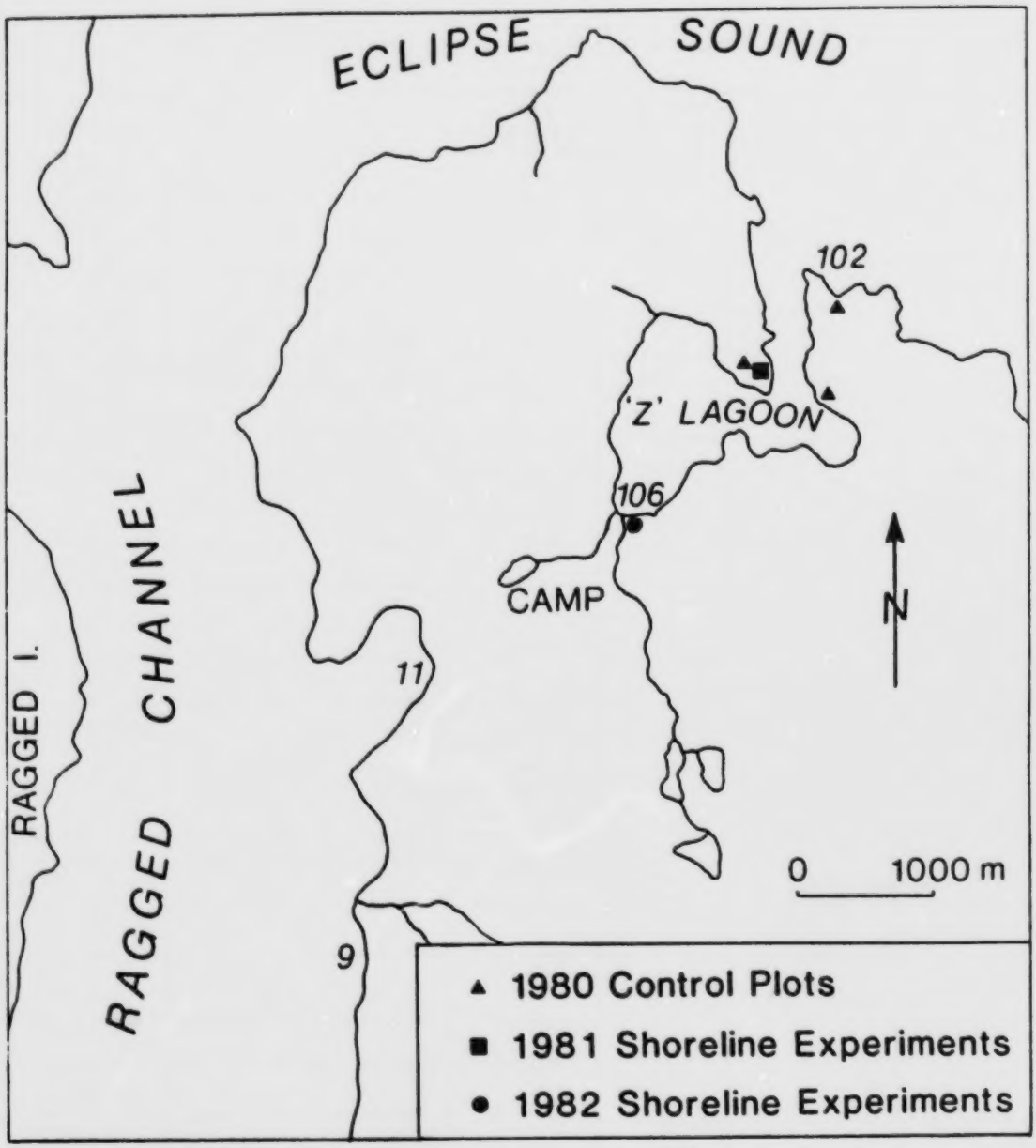


Figure 1.2 Location of "Z-Lagoon" study sites and of Bay 11.

terms of the character and distribution of the intertidal oil. It is hoped that the data set that was collected during 1985 can be enhanced by future, limited scale, surveys, even if these are not on an annual basis.

2.1 Introduction

Samples were collected from the two backshore control plots (T-1 and T-2) at Crude Oil Point (Figure 2.1) which were established in 1980. These surface and subsurface sediment samples were analysed for total hydrocarbon content and by gas chromatography.

No samples were collected from the high-energy intertidal control plots (H-1 and H-2) in Bay 102, as this site was considered to have been free of oil during the 1982 and 1983 studies. The site was visited but no intertidal oil was evident. Samples were collected from the low-energy intertidal control plots (L-1 and L-2) in Bay 103 (Figure 2.1). These samples were analysed for total hydrocarbon content and by gas chromatography.

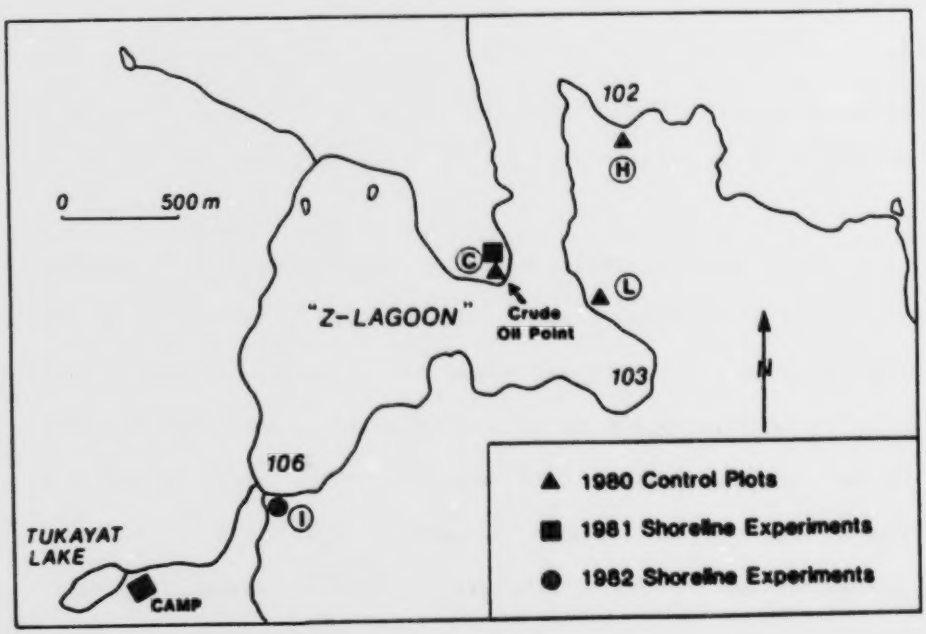


Figure 2.1 Control and experimental locations in the "Z-Lagoon" area. The letters correspond to the site codes described in Table 1.1.

2.2 1980 Backshore Control Plots.

An aged crude oil plot (T-1) and a water-in-aged crude oil emulsion plot (T-2) were established above the high-water limit at Crude Oil Point during 1980. It was evident from observations during the 1985 survey that these two plots had undergone relatively little visual change since 1983. The plots continue to have a surface of dark, weathered oil (Figure 2.2). Excavation for the collection of the samples exposed a black, oil-sediment mixture with a relatively fresh appearance (Figure 2.3).

Samples were collected at four locations from the surface and subsurface of each of the two plots. The results of the total hydrocarbon analysis on samples collected over the period 1980 to 1985 are presented in Table 2.1. The range of values for the surface samples collected in 1985 on plot T-1 is 13,000 to 20,000 mg/kg and for plot T-2 the range is 5,000 to 18,500 mg/kg. The range of values for the subsurface samples on plot T-1 is 1,100 to 11,100 mg/kg. and on plot T-2 is 4,100 to 12,600 mg/kg.

On plot T-1 the significant decrease in total hydrocarbon concentrations that occurred between 1982 and 1983 is reinforced by the 1985 data set. The highest value for a surface sample on this plot in 1985 is 19,900 mg/kg., considerably lower than the mean values obtained between 1980 and 1982. Similarly on plot T-2 there has been an apparent reduction in the oil in sediment concentrations in 1985 as compared to the 1981 through 1983 data.

Figure 2.2 Aerial view of backshore plots at Crude Oil Point (8 August, 1985). Arrow indicates the location of the 1981 test plots.

Figure 2.3 Close-up view of backshore control plots. Arrow indicates a small pit created by sample collection (11 August, 1985): c.f., Figure 2.3 in Owens (1984a).

Table 2.1 Total Hydrocarbon Content of Backshore Control Plot Samples (mg/kg).

DATE	1980				1981		1982		1983*	1985*
	20 Aug	22 Aug	24 Aug	28 Aug	28 July	29 Aug	10 Aug	2 Sept	20 Aug	11 Aug
T-1 (C) surface	40,100	58,300	33,800	65,800	28,400	34,000	28,300	28,700	8,775	15,750
subsurface	23,200	30,000	35,000	17,100	24,300	21,000	15,800	14,700	9,475	5,450
T-2 (E) surface	13,100	19,700	12,700	60,000	14,400	16,000	16,700	17,800	22,500	10,675
subsurface	15,400	27,100	13,300	58,100	20,600	18,000	16,800	13,500	5,917	6,225

C: Crude Oil

E: Emulsion

*: Mean of 4 values

Table 2.2 Amount of Initial Oil Remaining in Backshore Control Plot Samples on Selected Dates (%).

DATE	1980		1981	1982	1983	1985
	20 Aug	28 Aug	29 Aug	2 Sept	20 Aug	11 Aug
T-1 (C) surface	100%	164	85	72	22	39
subsurface	100%	74	91	63	41	23
T-2 (E) surface	100%	458	122	136	172	81
subsurface	100	377	117	88	38	40

C: Crude Oil

E: Emulsion

In neither case is there an evident explanation as the physical appearance of the plots was similar at each sample interval and the plots remained above the limit of marine action throughout the entire period of observations and samples. These trends are also evident when the data is viewed in terms of the amount of oil remaining by comparison to the initial total hydrocarbon values (Table 2.2).

Although it is inappropriate to attempt to derive too much information from the surface sample results over the five year period,it would appear that the total hydrocarbon concentrations on the crude plot (T-1) were (i) initially reduced from the high

values of between 34,000 and 66,000 mg/kg in 1980 to a range of between 28,000 and 34,000 in 1981 and 1982 and (ii) reduced again to a range of 9,000 to 16,000 in 1983 and 1985 and that this may represent a long-term trend. Data from the emulsion plot appears to be more consistent as all of the values, except for that of 28th August, 1980, fall within the range of 10,000 to 22,000 mg/kg.

Results from the analysis of the 1985 subsurface samples on T-1 yield a mean value of 5,450 (Table 2.1) and a range in values of 1,140 to 11,114 mg/kg. The results from T-2 yield a mean value of 6,225 with a range of 4,100 to 12,600 mg/kg. The subsurface data show a consistent slow reduction in the mean value over the five year period. On the crude plot (T-1) the 1980 values range between 17,000 and 35,000, since which time they have reduced progressively from 1981 to 1985. The 1985 concentrations are on the order of one-quarter of the 1981 values. Subsurface samples from the emulsion plot (T-2) show a similar trend in terms of the actual values and of the consistent slow decrease in total hydrocarbon concentrations. The 1985 concentrations are about one-third the 1981 values. These trends appear real and it is therefore assumed that there has been a steady decrease in the subsurface hydrocarbon concentrations through time. This decrease may be due to leaching effects.

Table 2.3(a) Saturated Hydrocarbon Weathering Ratio (SHWR) Values from Backshore Control Plot Samples (surface 1980-1983: surface and subsurface 1985)

	SURFACE						SUBSURFACE
	1980 (initial)	(+ 8 days)	1981	1982	1983	1985	1985
T-1 (Crude)	2.4	2.2	1.6	1.6	1.1	1.6	1.9
T-2 (Emulsion)	1.9	1.8	1.6	1.3	1.4	1.1	2.2

Table 2.3(b) Alkane/Isoprenoid Ratio (ALK/ISO) Values on Backshore Control Plots (surface 1980-1983: surface and subsurface 1985).

	SURFACE					SUBSURFACE
	1980	1981	1982	1983	1985	1985
T-1 (Crude)	2.4	3.0	2.1	2.4	1.9	2.0	2.1
T-2 (Emulsion)	2.6	2.3	2.4	2.4	2.2	1.8	2.2

It would be expected that the surface samples would reflect a more active series of weathering processes than would the subsurface samples. Although the surface and subsurface oils on both plots appear to have been relatively stable following 1980 there is an apparent slow but real trend that reflects a loss of hydrocarbons due to physical and/or biochemical weathering.

Results of the geochemical analyses of the surface and subsurface sediment samples collected in 1985 indicate that the subsurface hydrocarbons have undergone slower rates of evaporative weathering than have the hydrocarbons in the surface sediments (Table 2.3(a)). From a comparison with the data from previous years it is evident that the saturated hydrocarbon weathering ratio (SHWR) has been consistently low following the initial sampling period in 1980. The alkane/isoprenoid (ALK/ISO) values yield little meaningful information, either in the context of the data set from 1980 through 1985 or from comparison of surface and subsurface data obtained from the 1985 samples (Table 2.3(b)).

2.3 1980 Low Energy Intertidal Control Plots (L-1 and L-2)

Surface and subsurface samples were collected on the crude oil plot (L-1) in the upper, middle and lower sections of the plot. The data (Table 2.4) show that the trends evident in previous years continued to 1985. Although there remains some oil in the upper left corner of this plot (Photo 2.4) the surface total hydrocarbon values decreased in all three sections that were

Table 2.4 Total Sediment Hydrocarbon Content, low-energy Intertidal Control Plots (L-1 and L-2);
(a) oil-in-sediment values
(b) amount of oil remaining in 1982, 1983 and 1985 compared to initial oiling (%)

(a) Plot L-1 Aged Crude, Low Energy

		1980		1981		1982		1983	1985
	DATE	21 Aug	29 Aug	28 July	29 Aug	10 Aug	2 Sept	20 Aug	11 Aug
UPPER	surface	6,700	5,700	4,790	2,520	2,150	2,580	1,200	624
	subsurface	8,800	12,600	5,770	5,390	15,700	8,480	23,000	3,627
MIDDLE	surface	8,700	7,700	2,920	1,090	1,750	11,500	280	17
	subsurface	13,000	18,300	7,470	4,690	9,830	13,200	1,900	106
LOW	surface	36,000	6,000	6,460	1,290	5,540	440	400	29
	subsurface	24,600	10,800	1,820	4,510	3,030	3,840	730	270

(b)

1982	1983	1985
29 Aug	20 Aug	11 Aug
38	18	9
96	260	41
132	3	0.2
101	15	0.8
1	1	<0.1
15	3	1

Plot L-2 Emulsion, Low Energy

UPPER	surface	1,300	370	70	170	0	0	20	-
	subsurface	500	20	tr	190	0	0	0	-
MIDDLE	surface	4,500	10	290	170	0	40	0	11
	subsurface	2,200	160	130	160	0	0	0	20
LOW	surface	3,700	10	50	100	230	0	0	-
	subsurface	-	50	70	130	0	0	0	-

0	1.5	-
0	0	-
0.9	0	0.25
0	0	0.9
0	0	-
-	-	-

sampled. There was a similar decrease for all samples at all levels from the subsurface data set. The plot is visually oil-free except in the upper section where surface oil has been visible and where the subsurface sediments have retained a high concentration of hydrocarbons since the initial oiling.

Two samples were collected from the middle section of the emulsion plot (L-2) and these show very low hydrocarbon concentrations. This is consistent with the previous years' data sets which indicate that this plot was essentially clean by the 1982 sample period.

Figure 2.4 Low-energy intertidal plot in Bay 103 (8 August, 1985).

Table 2.5(a) Saturated Hydrocarbon Weathering Ratio (SHWR) Values on the Intertidal Control Plots

	1980 (INITIAL)	1980 (+ 8 days)	1981	1982	1983	1985 Surf	1985 Subs
L-1 (C)	2.5	2.5	1.1	1.3	1.1/1.0	1.0	1.2
L-2 (E)	2.1	2.0	1.0	1.1	1.3	1.2	1.5

Table 2.5(b) Alkane/Isoprenoid Ratio (ALK/ISO) Values on the Intertidal Control Plots

	1980 (INITIAL)	1980 (+ 8 days)	1981	1982	1983	1985 Surf	1985 Subs
L-1 (C)	2.4	2.5	1.9	1.7	0.9/1.7	0.15	0.5
L-2 (E)	2.7	2.8	1.1	1.1	1.7	3.6	2.3

Surface and subsurface samples from each plot were also analysed to determine the characteristic weathering ratios. The saturated hydrocarbon weathering ratios (Table 2.5(a)) for all four samples range between 1.0 and 1.5, with the subsurface values in each case being slightly higher than the surface values. The alkane/-isoprenoid ratios (Table 2.5(b)) show very low values on the crude oil plot (L-1) as might be expected, and unusually high values on the emulsion plot (L-2) in comparison to previous years' data.

2.4 Summary

2.4.1 Backshore Plots (T-1 and T-2)

Although the plots had changed little from previous years visually, the analytical results reveal significant changes over the 1980 to 1985 study period. Section 4.4(a) provides summary points that compare these backshore plots with those in Bay 106.

(a) Visual Character

- surface oil appeared weathered (dark grey) as in 1983; prior to 1983 it had a darker (black) and more fresh appearance
- subsurface oil was still black and had a fresh appearance in 1985

(b) Surface t-h Data

- on T-1 (crude) the 1985 mean (16,000 mg/kg) is about one-third of the 1980 mean (50,000 mg/kg), and the highest single 1985 value (20,000 mg/kg) is lower than all values up to and including the 1982 data set: this shows that there has been a real reduction in surface total hydrocarbon concentrations
- on T-2 (emulsion) the 1985 mean (10,700 mg/kg) is slightly lower than the means for 1981 through 1983 (range 14,400 to 22,500 mg/kg) but is half of the mean for the 1980 samples (26,400 mg/kg): although the trend is less evident than on the crude plot there does appear to have been a reduction in surface total hydrocarbon concentrations over time

(c) Subsurface t-L Data

- both plots exhibit a slow but continuous decrease from means of 22,650 mg/kg (T-1) and 30,200 mg/kg (T-2) in 1981 to means of 5,500 and 6,200 mg/kg respectively in 1985
- the 1985 means show a decrease to less than one-quarter of the 1980 means on both plots; there is therefore a clear trend of reduced total hydrocarbon concentrations over time

(d) Diagnostic Weathering Ratios

- the SHWR ratios for the surface samples show an initial lowering of values to 1981, since which time they have been stable

- the SHWR ratios for the subsurface samples collected in 1985 suggest that evaporative weathering rates have been slower than in the surface oiled sediments

- the ALK/ISO ratios show no discernable trends through time or between plots

2.4.2 Low-Energy Intertidal Plots (L-1 and L-2)

- some visible oil remains on L-1 (crude) covering a smaller area than was observed in 1983

- the L-1 total hydrocarbon values indicated a continued decrease in concentrations for both surface and subsurface sediments at all three levels: only the subsurface sample from the highest level produced a value above 1,000 mg/kg.

- two samples from the L-2 (emulsion) plot indicate that this plot remains initially oil-free

- the SHWR values have been low since the first year (1980) but the 1985 data suggest that subsurface evaporative weathering rates have been slightly lower than those in the surface sediments

- the ALK/ISO ratios show low values on L-1 but unusually high (and inexplicable) values on the L-2 (emulsion) plot when compared to previous years

3.1 Introduction

A series of countermeasure experiments were conducted on crude and emulsion plots at Crude Oil Point in 1981. In previous field seasons detailed sampling was undertaken to evaluate the initial and long-term changes associated with these countermeasures. Control plots were established to provide a standard data set against which the countermeasure plots could be compared. In this study no attempt was made to resample the entire set of plots as dispersion and sediment transport effects have resulted in considerable mixing and redistribution of the sediments. However a set of samples were collected on the two control plots (CC and CE), on the two mixing plots (MC and ME), which showed elevated hydrocarbon values in 1983, and on one of the dispersant plots (D(E)E) (Figure 3.1).

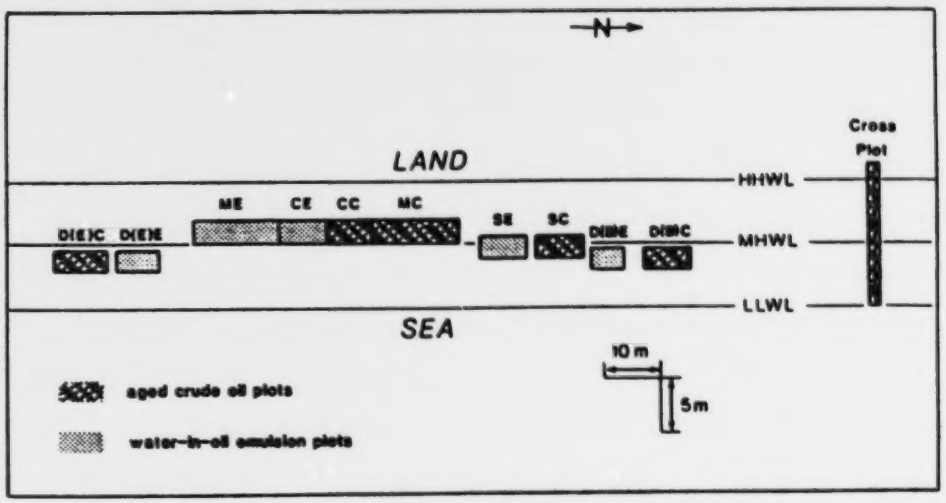


Figure 3.1 Location and layout of 1981 countermeasures experiment and control plots at Crude Oil Point. The location of the plots is shown in Figure 2.1 and the plot identification codes are given in Table 1.1.

Trace amounts of visible oil were present in the vicinity of the highest high-water mark on the southern section of the beach. These were typically in the form of pebbles with a thin coating of weathered oil. A patch of oil was still very visible at the location of the 1981 test plots, adjacent to the two backshore control plots (Photo 2.2). This patch of oil in the relatively sheltered southern section of Crude Oil Point appears to have altered very little since August 1982 (see Figure 3.5 in Owens et al 1983).

3.2 Total Hydrocarbon Analysis Results

The results of total extractable hydrocarbons from the samples collected in 1985 are compared to the previous results in Table 3.1. The subsurface sediments on the MC plot have retained elevated concentrations of total hydrocarbons throughout the period of observations. During the sample collection in 1985 the oil from the subsurface of the sediments appeared as a dull weathered residue. This is the only site at which oil was evident, other than on the pebbles above the highest high-water mark. Samples from the other plots retain background levels of hydrocarbons which indicate that there are small residues left as a result of the experiments that were conducted on this beach.

The conclusion that can be drawn from this limited number of samples is that the mixing technique resulted in burial of the surface oil to depths below which wave action has sorted and redistributed the sediments over the period 1981 through 1985.

Table 3.1 Results of Total Extractable Hydrocarbon Analyses - 1981 Countermeasures Control and Experimental Plots (mg/kg).

CODE		1981				1982		1983	1985
		Pre-Test	Post-Test	Aug 15 + 8 days	Sept 16 + 40/41 days	Aug 10	Sept 02	Aug 20	Aug 11
CC	surface	21,000	*	17,000	3,110	300	80	22	19
	subsurface	3,020	*	1,500	150	3,380	220	430	73
CE	surface	12,000	*	21,700	930	90	500	21	19
	subsurface	1,060	*	380	110	390	300	190	69
MC	surface	21,000	28,000	4,980	19,000	160	140	32	470
	subsurface	3,020	10,000	16,000	1,800	1,240	2,280	3,200	8,000
ME	surface	12,000	21,000	19,000	1,890	230	100	20	31
	subsurface	1,060	290	310	190	1,070	450	84	1,500
D(E)E	surface	24,000	20,000	2,370	330	130	370	0	9
	subsurface	150	513	290	tr	170	260	120	59

Table 3.2(a) Evaporative Weathering Ratio (SHWR)

	1981			1982		1983	1985
	Post-Test	+8 Days	+40 Days	8 Aug	29 Aug	17 Aug	11 Aug
CC surface	3.0	2.6	1.6	1.3	1.1	3.3	1.4
subsurface	-	-	-	-	-	2.0	1.5
CE surface	3.0	2.3	1.4	1.1	1.0	2.0	1.4
subsurface	-	-	-	-	-	1.9	1.8

Table 3.2(b) Biodegradation (Alkane to Isoprenoid Ratio)

CC surface	2.1	2.6	1.6	2.2	1.6	3.2	2.1
subsurface	-	-	-	-	-	0.7	1.7
CE surface	2.7	2.6	2.7	1.6	1.5	2.1	1.1
subsurface	-	-	-	-	-	1.4	2.0

3.3 Geochemical Analyses

The 1985 saturated hydrocarbon weathering ratios for the intertidal two control plots (Table 3.2(a)) indicate relatively low values on the surface of both plots with slightly higher subsurface values. These ratios are in the same order as those from 1981 and 1982, and it appears that the 1983 surface samples are affected by some unknown artifact, possibly such as spilled gasoline from hunters who regularly use this beach during the summer open-water season.

The alkane/isoprenoid ratios (Table 3.2(b)) yield little information. There appears to be no long-term discernible trend in the surface values, as these have fluctuated from one survey period to the next. In addition there is no apparent trend between the subsurface and surface biodegradation rates.

3.4 Summary

A small number of samples were collected at locations which yielded high hydrocarbon content values in 1983. The results show that some intertidal oil still remains in the fifth open-water season on this partially exposed beach.

- patches of oiled pebbles and cobbles were visible at the highest high-water mark adjacent to the mixed and control plots
- a thick patch of oil was still present at the high-water level at the test plot sites on the more sheltered south-facing beach at Crude Oil Point
- significant hydrocarbon concentrations remain in the subsurface sediments at the two mixed plots (MC and ME), with values of 8,000 and 1,500 mg/kg respectively
- only one surface sample (MC) had a value above 30 mg/kg.
- the mixing action in 1981 on the intertidal plots buried oil to a depth below the normal level of wave action on this beach
- the diagnostic weathering ratios from the intertidal control plots (CC and CE) samples collected in 1985 yield little information; but do confirm that the 1983 surface ratios were probably anomalous

4.0 BIOS 1982 COUNTERMEASURES EXPERIMENTS

4.1 Introduction

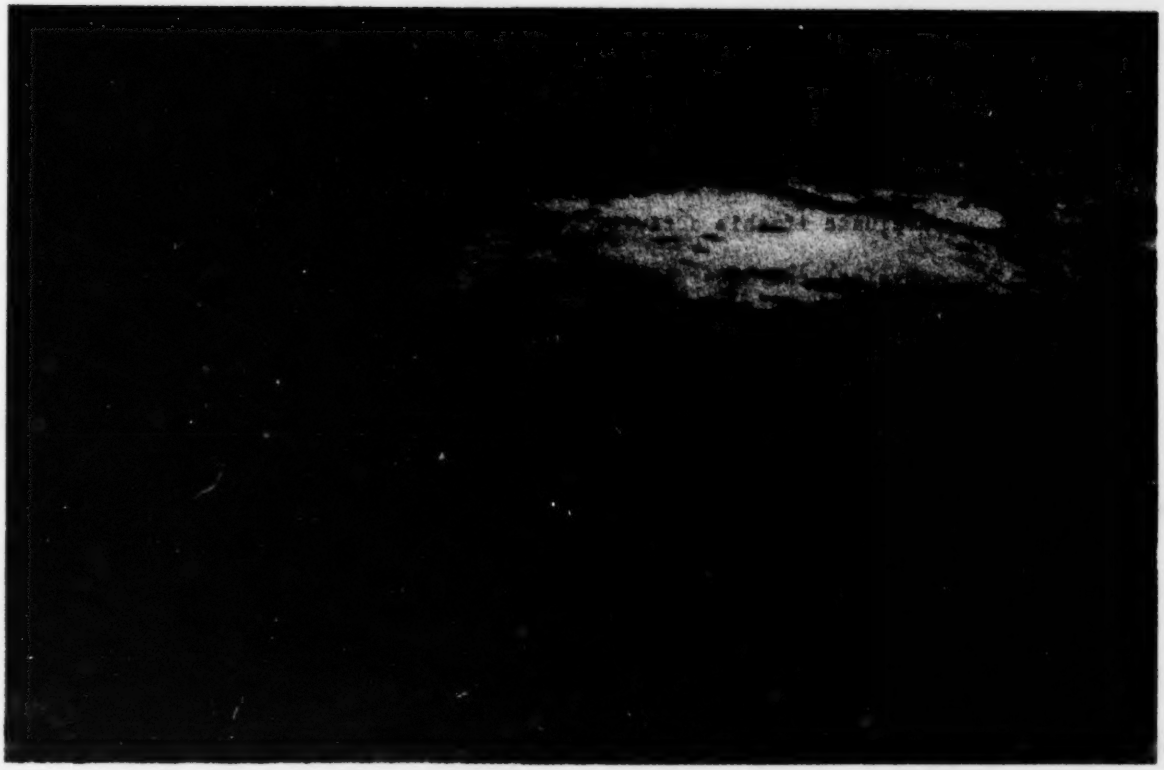
The purpose of the 1985 investigations was to sample, analyse and evaluate the effects of the backshore mixing experiments on the upper beach in this very sheltered part of Bay 106. The site had been unaffected by marine processes and a complete suite of surface and subsurface samples was collected for total extractable hydrocarbon and for GC/MS analyses. The plots have not been affected by marine processes so that this data set can be compared with results from the 1982 and 1983 surveys.

Bay 106 is located in the innermost part of Z-Lagoon (Figures 1.2 2.1, and 4.1). Backshore plots of the crude and emulsified oil were laid down on the beach berm and landward of the berm to replicate oil that would have become stranded during a period of storm high-water levels in a very sheltered, low-energy environment. One half of each plot was then mixed with a roto-tiller to evaluate if this activity would have any beneficial affect on the physical character of the stranded oil.

4.2 Backshore Plots - Total Hydrocarbon Analysis Results

The results of the analyses from the 1985 survey, when compared to the previous data sets (Figures 4.2 and 4.3; Table 4.1), indicate that after some initial variability during the first year of the experiment (1982) the mean value of total extractable hydrocarbons on the surface of the control plots decreased from

(a)



(b)

Figure 4.1 Aerial views of Bay 106 backshore crude (IMC) and emulsion (IME) plots; c = control; m = mixed. The two other backshore plots to the right of the IM plot in the lower photograph were used for separate studies (8 August, 1985).

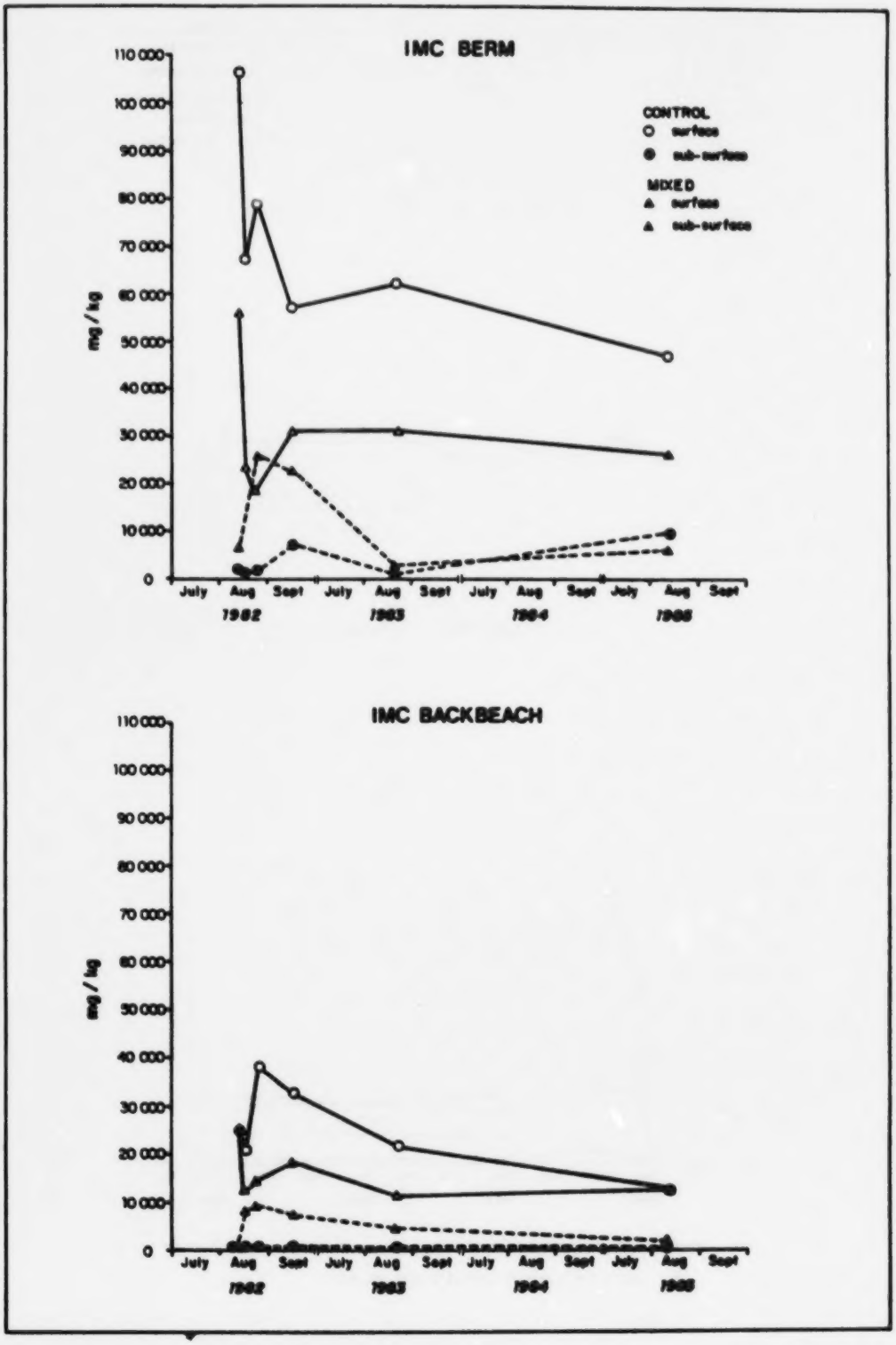


Figure 4.2 Bay 106 total hydrocarbon oil-in-sediment values (mg/kg).
(a) crude oil plot

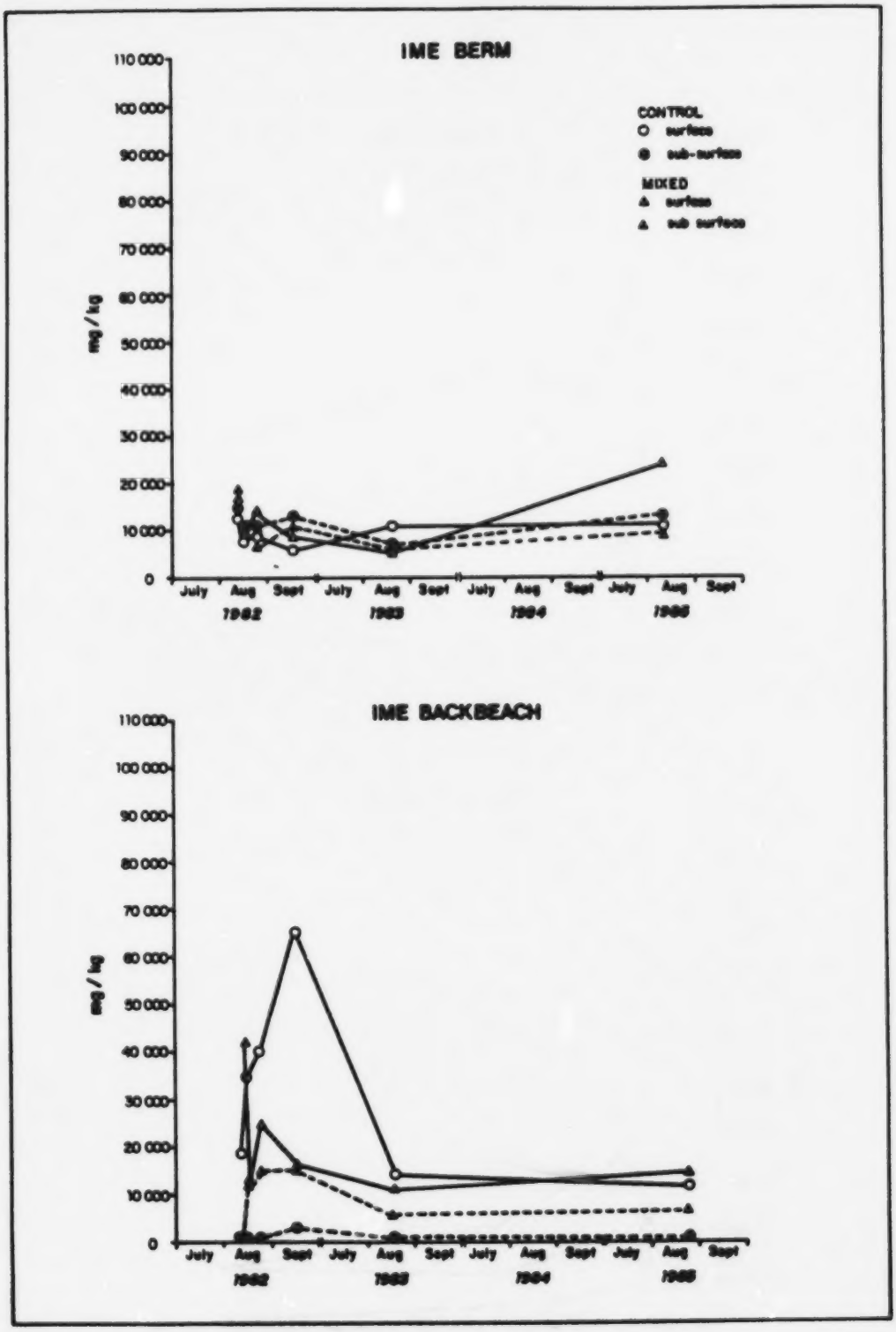


Figure 4.2 (b) water-in-oil emulsion plot.

Table 4.1 Total Hydrocarbon Results (mg/kg) for Bay 106 Backshore Plots

(a) surface

		1982				1983	1985
		Pre-Test 14 Aug	Post-Test 15 Aug	22 Aug	15 Sept	20 Aug	10 Aug
IMC	control berm	106,000	66,900	88,600	57,100	62,000	47,000
	control back beach	23,800	20,600	38,200	32,600	22,000	12,500
	mixed berm	56,500	23,200	18,700	31,100	31,000	25,900
	mixed back beach	24,200	12,700	14,500	18,200	11,000	12,500
IME	control berm	12,400	7,730	8,640	5,350	11,000	11,300
	control back beach	18,400	34,500	40,000	65,200	14,000	11,800
	mixed berm	17,100	9,270	13,800	8,510	7,400	24,200
	mixed back beach	42,200	12,300	24,800	16,700	11,000	15,300

(b) subsurface

		1982				1983	1985
		Pre-Test 14 Aug	Post-Test 15 Aug	22 Aug	15 Sept	20 Aug	10 Aug
IMC	control berm	2,200	1,420	1,860	7,380	930	9,700
	control back beach	100	570	170	590	480	60
	mixed berm	7,010	-	26,900	22,500	2,300	6,200
	mixed back beach	270	8,400	9,400	7,510	4,500	1,800
IME	control berm	14,500	11,200	11,500	12,800	7,100	12,300
	control back beach	140	120	220	3,050	280	37
	mixed berm	17,900	12,600	7,670	11,500	7,800	9,400
	mixed back beach	360	11,900	15,100	15,100	5,500	7,300

37,000 mg/kg in 1982 to 20,000 mg/kg in 1985 (Table 4.2(a)). The surface values have been relatively stable in the 1983 and 1985 data sets. The values from the subsurface samples on the control plots were very consistent over the entire study period. Both back beach sections of the control plots showed values generally less than 500 mg/kg, with only one value above 500 mg/kg (Table 4.1(b); Figures 4.2 [a and b]). The values are higher on the berm section due to the higher porosity of the berm sediments, however the mean value of all samples from the control plots subsurface sediments was in the order of 5,300 in 1982 and remained at that level with a value of 5,500 in 1985.

These results are not unexpected and are in line with results from the backshore control plots at Crude Oil Point. As an item of contrast the 1985 mean value of subsurface total hydrocarbons values from the control plots in Bay 106 is 5,500, this compares with the value of 5,400 for the subsurface sediments on plot T-1 (Table 2.1) and a value of 6,200 for plot T-2. The combined surface values from T-1 and T-2 yield a mean of 13,200 mg/kg which compares to the mean value of Bay 106 surface sediment control plots of 20,000 mg/kg (Table 4.2). These figures are of interest primarily because they show a simple consistency between the two experiments at different locations in Z-Lagoon.

Table 4.2 Mean Values of Total Extractable Hydrocarbons

	(a) Bay 106				(b) Crude Oil Point (T1 and T2)
	1982 Pre-test	1982 Post-test	1983	1985	1985
CONTROL PLOTS - surface sediments	37,575	-	27,250	20,650	13,212
MIXED PLOTS - surface sediments	-	14,367	15,100	19,475	-
CONTROL PLOTS - subsurface sediments	5,310	-	2,197	5,524	5,837
MIXED PLOTS - subsurface sediments	-	10,966	5,025	6,175	-

The mixing experiments yielded results which will be dealt with initially on a plot-by-plot basis, and then considered in the overall context. On the crude oil plot (IMC) the surface total hydrocarbon values on the berm section were considerably reduced by the third sample interval (15 Sept 1982) (Figure 4.2[a]). This value remained relatively constant in the 1983 and 1985 data. The value of 31,000 mg/kg is approximately half of the value from the berm of the adjacent control crude oil plot. The subsurface samples from the berm area of IMC in 1985 have produced higher values in the control subsurface sediments than in the mixed subsurface sediments. However, it would be inappropriate to conclude that the mixing therefore had a beneficial effect in lowering the total hydrocarbon values in the subsurface sediments as the difference between the two values is relatively small (9,700 versus 6,200 mg/kg).

On the backbeach section of the crude oil plot the surface total hydrocarbon values after three year are virtually identical (12,500 mg/kg). It would appear therefore that surface mixing did not significantly improve the condition of the stranded oil on the backbeach, in terms of the hydrocarbon content of the sediments, but this must be offset by the considerable improvement in the visual character of the surface of the plot (Figures 4.1 and 4.3). The backbeach of the mixed plot has a surface that is more acceptable in terms of the visual aspects of contamination and probably more acceptable in terms of the adherence of

Figure 4.3 Close-up of Bay 106 backshore crude plot (IMC), the sea is to the right; c.f., Figures 4.7 and 4.8 in Owens (1984a) - note that the 1983 figures are incorrectly labelled.

oil to animals or birds that might cross the plots. The subsurface total hydrocarbon values on the mixed backbeach section of IMC were elevated by the mixing activity as compared to the control plot subsurface sediments. After an initial period of high values in the order of 7,500 to 9,500 mg/kg in 1982, the concentrations have decreased over the subsequent three-year period to a level similar to that in the backbeach control subsurface sediments.

On the emulsion plot (IME) relatively small volumes of hydrocarbons were initially retained on the berm section (Figure 4.2[b]). The surface and subsurface total hydrocarbon volumes on the berm section remained relatively constant throughout the entire study period with no significant difference in the concentrations of the subsurface versus the surface sediments. The mixing activity on these emulsion plots does not appear to have had any significant effect with regard to the total hydrocarbon concentrations of either the subsurface or surface sediments. In fact the 1985 results indicate a considerably higher concentration on the mixed berm plot as compared to the control berm plot. Again mixing appears to have had little major beneficial effect in reducing total hydrocarbon concentrations or volumes.

On the backbeach section of this emulsion plot there is little difference between the concentrations of the control and mixed sediments in the 1983 and 1985 results. The subsurface sediments of the backbeach section show a marked increase following the 1982 tests and elevated concentrations can still be identified in the 1985 data set (Figure 4.2[b]). In the backbeach area mixing again does not appear to have improved the contamination (i.e. reduced the total hydrocarbon concentration) and there is good evidence for an increase in contamination in the subsurface backbeach sediments.

Considering the data set as a whole (Table 4.2), three years after the experiment there is no difference between the total hydrocarbon concentrations on the control or mixed plots, for either the surface or subsurface sediments. This result is not altogether surprising as the primary effect of the mixing procedure was to encourage physically evaporative weathering. These weathering processes were accelerated on the mixing plots but after three years the untreated control plot hydrocarbons had undergone the same processes albeit at a slower rate.

The consistency of this conclusion is supported by a comparison of the results of the surface and subsurface analysis of the backshore control plots at Crude Oil Point (T1 and T2) which show total hydrocarbon concentration values similar to those from the Bay 106 backshore plots. The lesson that can be drawn from this data set is that mixing has a potential value in the initial stages following an oil spill, but that in the long run (i.e. over a three-year period) mixing has little value in reducing hydrocarbon concentrations. The primary benefit of undertaking mixing is to make the surface physical character of the contaminated site more acceptable in terms of visual or traffic considerations rather than to reduce the amounts of oil above the high-water level.

4.3 Backshore Plots - Geochemical Analysis Results

The saturated hydrocarbon weathering ratios (Table 4.3(a)) show a very strong consistency within the surface data on both control and mixed plots in both 1983 and 1985 sample periods. Similarly there is a uniformity in the subsurface ratios for both control and mixed plots in both sample periods. The interesting point is that the mixing did not have any long-term impact on the degree of physical weathering by evaporation.

The alkane/isoprenoid ratios (Table 4.3(b)) indicate that biodegradation has been more active on the control plots than on the mixed plots. Again there is a marked uniformity within the control surface and subsurface data and separately within the mixed surface and subsurface data from both years. The general conclusion that can be drawn from this is that the mixing activity has reduced rather than enhanced the degree of microbial or biodegradation.

Intuitively it would have been expected that mixing would have increased the physical evaporative weathering. This may have occured during the 1982 period but no data are available to corroborate this concept. It is clear that by 1983 and 1985 physical evaporative weathering rates were the same within the

Table 4.3 Bay 106 Backshore Geochemical Analysis Results

(a) SHWR

	Control		Mixed	
	1983	1985	1983	1985
surface	1.5	1.6	1.6	1.7
subsurface	1.9	1.9	2.0	2.0

(b) ALK/ISO

	Control		Mixed	
	1983	1985	1983	1985
surface	1.9	1.9	2.3	2.2
subsurface	2.2	1.9	2.2	2.2

surface sediments and separately within the subsurface sediments of both plots. The only difference being that the subsurface physical evaporative weathering rates were slightly slower than those within the surface sediments. The remarkable uniformity of the alkane/isoprenoid ratios is interrupted by only one value (the 1983 subsurface control value) and the data set would indicate that biodegradation was slow on the mixed plots. Intuitively one would have expected the reverse situation, as larger surface areas of the stranded oil would have been exposed by the mixing plots. This however was not the case and there is no ready explanation for the higher biodegradation rates on the control plots.

4.4 Summary

The backshore plots had changed little in appearance from the 1983 observations and the geochemical analyses indicate that the plots were also relatively unchanged in terms of t-h concentrations and weathering characteristics.

(a) Control Plots - Total Hydrocarbon

- the surface t-h values in both control plots (IMC-c and IME-c) remained relatively unchanged between 1983 and 1985
- the subsurface t-h values on both plots show consistently similar values over the entire study period, with values higher by more than two orders of magnitude from the more porous berm subsurface sediments than from the backbeach sections
- the mean value of all 1985 surface control samples is 20,650 mg/kg as compared to a similar mean for the Crude Oil Point backshore controls (T-1 and T-2) of 13,200 mk/kg: the comparative subsurface values are 5,500 mg/kg for Bay 106 and 5,800 mg/kg for Crude Oil Point: there appears to be therefore a degree of consistency between these two backshore sites in "Z-Lagoon"

(b) Mixed Plots - Total Hydrocarbon

- in the third open-water season following the experiments there is virtually no difference between the mean t-h concentrations in the surface and subsurface sediments between the control and mixed plots (surface, 20,650 and 19,500 mg/kg respectively: subsurface 5,500 and 6,200 mg/kg respectively)
- the mixing initially accelerated natural physical weathering processes, but over the study period the untreated plots underwent the same processes and achieved the same results, albeit at a slower rate
- despite these similarities in oil concentrations the mixed plots appear to be physically improved in terms of (a) the visual amounts of surface oil ad (b) adherence of oil to animal or bird feet

(c) Diagnostic Weathering Ratios

- mixing does not appear to have had any long-term effect in lowering the SHWR values: subsurface physical evaporative weathering rates are slower then those for the surface sediments

- biodegradation (ALK/ISO ratio) appears to have been more active on the control rather than the mixed plots, so that mixing may have reduced rather than enhanced this weathering process

5.0 RAGGED CHANNEL SURVEYS - BAY 11

5.1 Introduction

The investigations carried out on the intertidal beach of Bay 11 represent an evaluation of the long-term fate and persistence of oil that became stranded following an experimental near-shore spill. The spill was designed to release oil adjacent to the shoreline so that that oil would become stranded and would enter the nearshore water-column. The field objectives of the shoreline component of the BIOS study were to sample the intertidal sediments for total hydrocarbon concentrations and to map the surface oil cover on the intertidal zone. These Bay 11 investigations were the primary impetus for returning to the Cape Hatt area in 1985 for shoreline studies. These investigations continue to yield valuable information and it is hoped that the data set will be further enhanced by future, small-scale, studies.

5.2 Intertidal Hydrocarbon Analysis Results

Two sets of samples were collected for total hydrocarbon analysis. The first set was collected systematically from the surface and subsurface of the upper, middle, and lower one-third of intertidal zone along profiles that had been previously sampled in 1981, 1982, and 1983. A second set of fourteen samples were collected at locations identified as providing meaningful information with regard to specific features (e.g.: the asphalt pavement). The three sample sets collected along profiles 1, 3, 6 and 7 are summarised in Table 5.1. The surface results indicate

Table 5.1 Summary of Bay 11 Total Sediment Hydrocarbon Values (mg/kg): based on a repeated sample pattern.

	1981			1982	1983	1985
	20 Aug (day 0)	28 Aug (day +8)	15 Sept (day +25)	10 Aug	16 Aug	9 Aug
upper intertidal	8,800	7,000	7,100	8,300	28,600	5,350
middle intertidal	3,800	8,000	6,800	3,000	6,000	1,912
lower intertidal	8,600	5,000	3,800	1,900	990	512
mean	7,100	6,600	5,900	4,400	11,870	2,601
upper intertidal	260	2,100	70	2,600	710	98
middle intertidal	90	290	310	310	1,280	968
lower intertidal	150	360	260	130	420	826
mean	170	900	210	1,026	1,284	631

that the pattern of decreasing values from the upper intertidal zone towards the lower intertidal zone which was evident in late 1981, 1982 and 1983 continued into the 1985 data set. The individual values for the three intertidal zones have decreased from previous sampling periods, as has the mean value for all surface sediment samples. These across-beach changes and the decreases in values through time are consistent with the continued physical weathering of the stranded oil.

The results from the subsurface sediment analyses yield less obvious trends. As expected the values are considerably lower than those for the surface sediments but the same across-beach trends are not evident. Although the mean value is lower than that for 1982/83 there are no trends through time for the three intertidal zones. It may be possible that there is an evident increase in the subsurface values for the lower intertidal area that reflects the movement of oil down the intertidal zone towards the low-water line within the sediments. However this is only speculative as the values themselves are low (less than 1,000 mg/kg).

Six surface sediment samples were collected from the asphalt pavement between profiles 3 and 11. The total hydrocarbon concentrations range from 12,000 to 25,000 mg/kg, with a mean value of 19,000 mg/kg. This compares with a mean of all beach-face surface samples collected in 1983 of 19,835 mg/kg. Three

samples from the lower intertidal zone ridge yielded values of 3,900, 6,400, and 24,400 mg/kg (a mean of 11,600 mg/kg). A sample on profile 6 from the area between the asphalt pavement and the lower intertidal ridge produced a value of 1,700 mg/kg. These general numbers of 2% oil-in-sediment by weight for the asphalt pavement, 1% for the lower intertidal ridge sediments, and on the order of 0.1% for the middle section correlate well with the interpretation provided by Owens et al (in press) based on the 1983 data set (Figure 5.1).

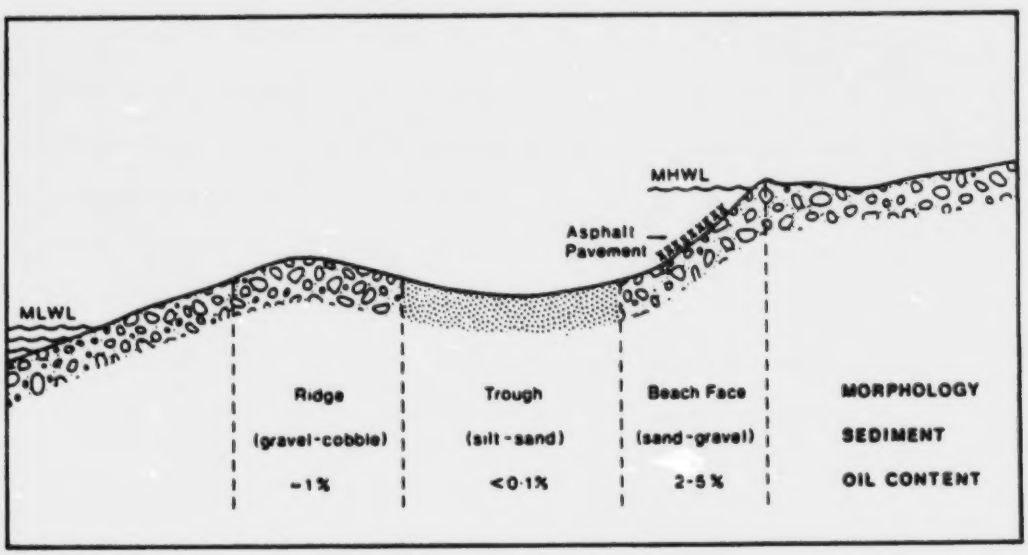


Figure 5.1 Schematic diagram of the relationship between oil concentrations (expressed as per cent oil-in-sediment by weight), sediment type and morphology along a profile line across the intertidal zone in Bay 11 (from Owens, 1984a).

Table 5.2 Geochemical Results from 1985 Bay 11 Samples

(a) Saturated Hydrocarbon Weathering Ratio

	n	mean	number of samples with ratio <1.25
20 Aug 1981	6	2.6	0
15 Sept 1981	6	1.6	1
8 Aug 1982	6	1.1	6
16 Aug 1983	12	1.2	9
9 Aug 1985	15	1.3	11

(b) Alkane/Isoprenoid Ratio

	n	mean	number of samples with ratio <1.00
20 Aug 1981	6	2.7	0
15 Sept 1981	6	2.6	0
8 Aug 1982	6	1.1	2
16 Aug 1983	12	1.1	6
9 Aug 1985	15	0.95	8

5.3 Intertidal Geochemical Analysis Results

The values for the saturated hydrocarbon weathering ratio (Table 5.2(a)) showed an initial rapid decrease in 1981 over a 25 day period, and again between 1981 and 1982. The low ratios have continued since 1982 and the only significant point that can be made for the 1982 through 1985 data set is that there has been an increase in the samples which have very low ratios (<1.25).

The alkane/isoprenoid ratio (Table 5.2(b)) similarly shows a rapid decrease from 1981 to 1982. Since that time the ratio has been relatively low and the only point of significance is again that the number of samples with low ratios (<1.0) has steadily increased over the period of investigations.

5.4 Surface Oil Cover Survey

A series of ground observations were carried out during the field survey in order to estimate the amount of oil that remained on the intertidal beach at Bay 11 (Figure 5.2). These observations were carried out along profile lines which had been surveyed in a similar manner in 1981, 1982, and 1983. As a result of these observations a series of maps have been produced that indicate the changes in the surface oil cover over the four-year period of observations (Figures 5.3 and 5.4). The oil that remains in the intertidal zone is concentrated in the upper third, on the beach-face slope. This oil is primarily in the form of an asphalt pavement that is up to 10cm thick and has a 75 - 100% cover on the beach surface (Figure 5.5). This asphalt pavement is a mixture of oil-in-sediments that was first evident in the 1983 survey. A second area of oil concentration is in the lower intertidal zone where a ridge of coarse material has a 50 - 100% oil cover on the ridge crest (Figure 5.6). These two areas are separated by a trough of fine-grained sediments which was partially oil-free at the time of the 1982 survey (Figure 5.1).

The total area of the beach that was covered by oil in 1985 is 4,400 m^2. This shows little change from the 1983 survey (Table 5.3). A detailed breakdown of the oil cover by category indicates that the character of the oil cover had changed little from 1983 to 1985. The average surface oil cover is reduced slightly from the 1983 data set (Table 5.4), but these variations are within the realm of measurement error so that it must be assumed that there has been no net change in the total area or in the character of the oil cover from 1983 to 1985.

Figure 5.2 Aerial view of Bay 11 on Ragged Channel - 8 August, 1985.

(a)

(b)

Figure 5.3 Bay 11 intertidal zone: (a) 14 August 1983.
(b) 8 August 1985.

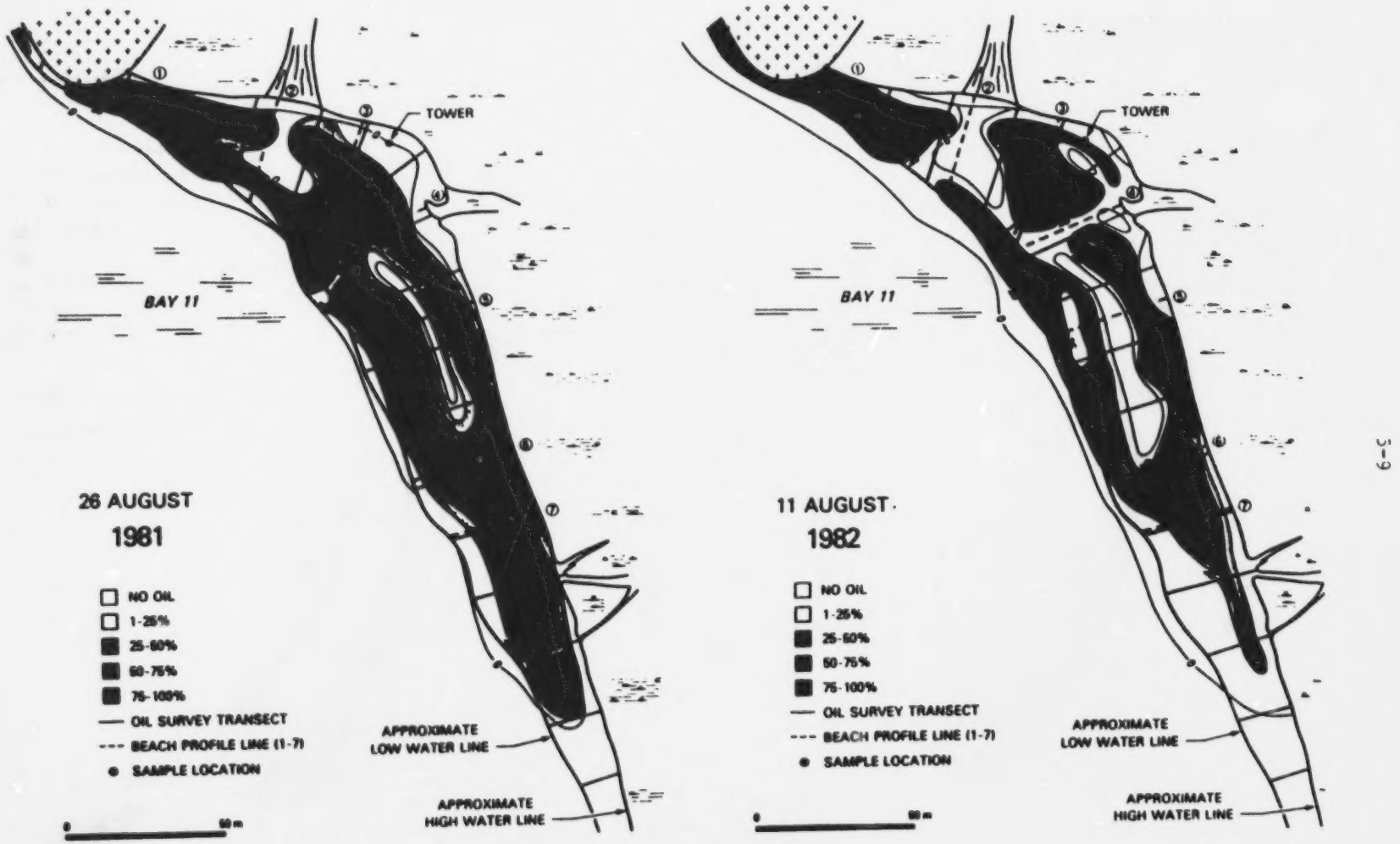
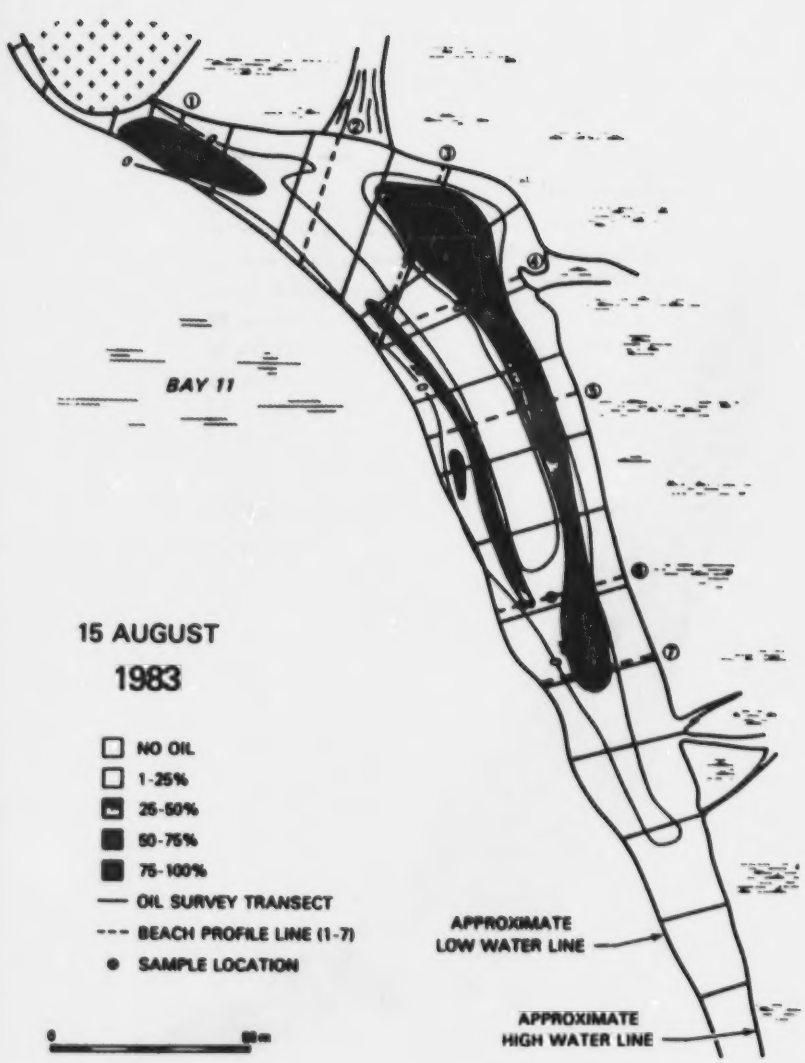


Figure 5.4 Surface oil distribution maps: (a) 26 August 1981
(b) 11 August 1982



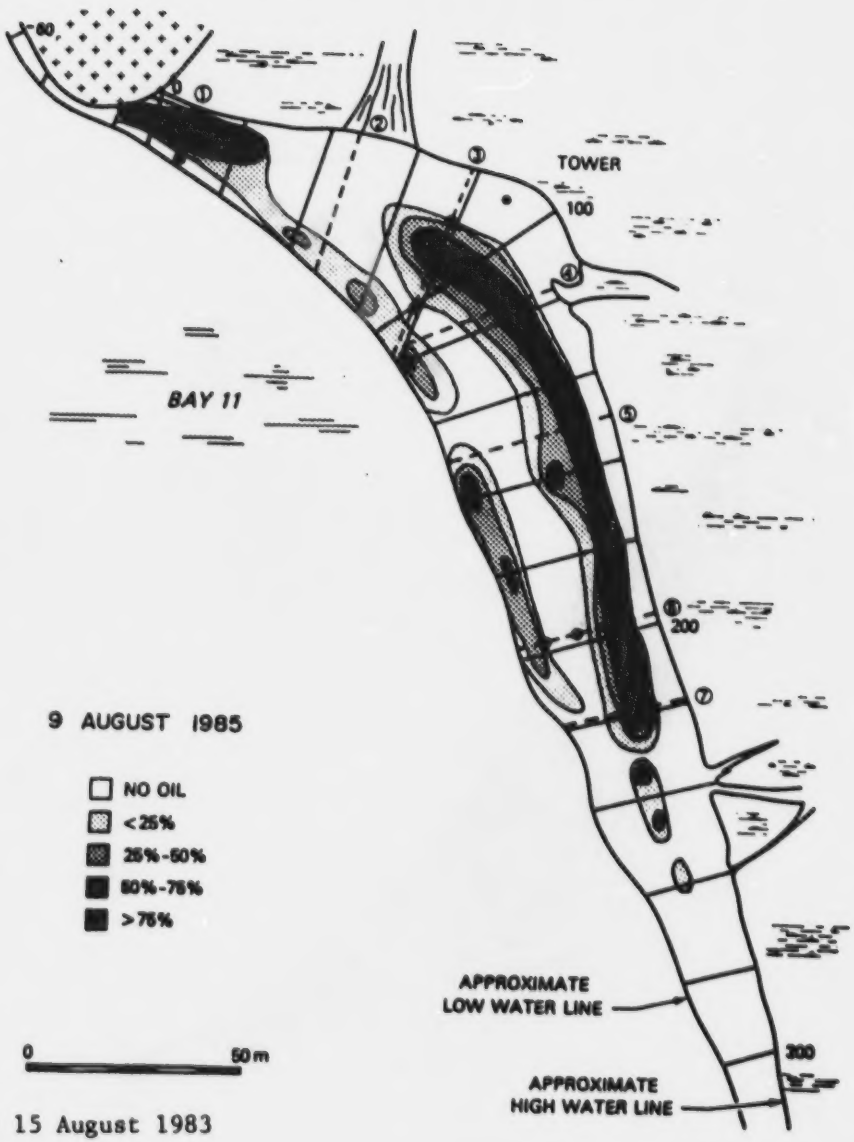


Figure 5.4 (cont'd): (c) 15 August 1983
(d) 9 August 1985.

Figure 5.5 Close-up of upper edge of the asphalt pavement at Profile 6 (Figure 5.4(d)), 9 August 1985. The scale is 25 cm in length.

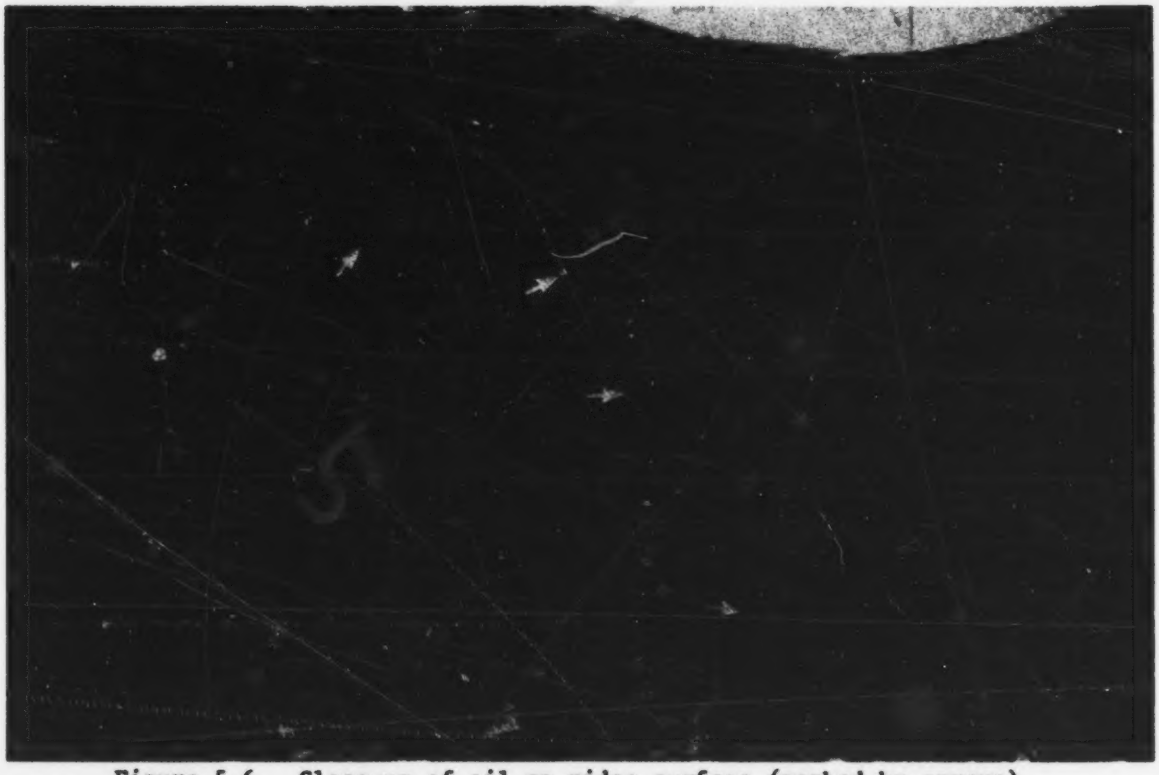


Figure 5.6 Close-up of oil on ridge surface (marked by arrows) in lower intertidal zone on Profile 6 (Figure 5.4(d)), 9 August 1985.

Table 5.3 Surface Oil Cover

	Surface Oil Cover by Category (m^2)				Total Area Oiled
Year	0.1 - 24%	25 - 49	50 - 74	75 - 100%	(m^2)
1981	2015	1700	1145	3710	8570
1982	5200	1775	1320	1305	9600
1983	2120	840	350	615	3925
1985	1830	1440	660	510	4400

Table 5.4 Changes in Estimated Oil Content of Beach 1981 - 1985

	Total Oiled Area (m^2)	Average Surface Oil Cover (%)	Equivalent Area of 100% Oil Cover (m^2)	Percentage of Beach Area Oiled (%)	Percentage of Initial Oil Remaining (%)
1981	8570	57	4850	58	100
1982	9600	34	3282	65	67
1983	3925	34	1337	25	28
1985	4440	27	1610	30	33

5.5 Estimated Oil Budgets

Two methods of estimating the volume of oil remaining in the beach sediments are described by Owens et al (in press). In essence the "area method" uses the mean value of the total hydrocarbon samples to obtain an oil concentration, by multiplying this value by the average sample weight. This concentration is converted to a volume by dividing by the assumed density of the oil (0.89) and this volume is then related to the area of oiled beach divided by the area of each sample to produce a total volume of oil on the beach.

The second method the "volume method" again uses the mean total hydrocarbon value. A volume is obtained by multiplying the area of beach that is oiled by the assumed sample depth (2cm) to give an oiled beach volume. The weight of the beach material is obtained by multiplying the volume by the density. This value is then multiplied by the oil concentration and then by the assumed density of oil. For the 1983 and 1985 data sets all surface samples obtained from the Bay 11 intertidal zone were used to obtain a mean total hydrocarbon value.

The computed oil budgets using the methods described above (Table 5.5) indicate that the volume of oil remaining in the surface sediments of the intertidal zone is virtually unchanged between 1983 and 1985. In light of the surface area of remaining oil

Table 5.5 Surface Total Hydrocarbon Concentrations and Computed Oil Volumes

DATE	Number of Samples	Mean of Surface Total Hydrocarbon (mg/kg)	Surface Oil Volume	
			Area Method	Volume Method
19th August, 1981	6	17,400	8.0m^3	6.7m^3
20th August, 1981	9	7,100	3.3	2.7
28th August, 1981	9	6,700	3.1	2.6
15th August, 1981	9	5,900	2.7	2.3
10th August, 1982	9	4,400	2.3	1.9
16th August, 1983	19	8,150	1.8	1.5
9th August, 1985	23	8,400	2.0	1.7

this figure is not totally unexpected, but it must be remembered that the volume computations are not dependant solely upon areal data but also include the total hydrocarbon concentrations as a variable. These volumes are at best a rough estimate of the real world volume of oil that remains in the beach. Nevertheless they do provide a general indication of changes through time when compared to the original volume of stranded oil.

Taking the asphalt pavement as a separate component, with a 100% oil cover on the surface that is 5cm deep, the "volume method" computations provide values of 0.7m^3 for 1983 and 0.3m^3 for 1985. As the hydrocarbon concentrations are similar between the two years this reduction in volume is due to the reduced surface area of the pavement.

5.6 Discussion

The beach at Bay 11 has been extensively surveyed from 1981 through to August 1985 to estimate changes in the oil budget for the intertidal zone. On first impression, in August 1985, the oil cover appeared to be considerably reduced from the 1983 survey. The results that were obtained therefore were initially surprising. Upon review the primary change between 1985 was not one of the oil cover or of the oil volume, but rather an increased surface weathering that changed the colour of the oil from a dark almost black colour to more subdued tones which blended with the beach sediments. As a result the initial visual estimates of the surface oil cover, not to be confused with the ground observations along the profile lines, suggested that there was less surface oil than in previous years. This is an important point as aerial or ground estimates are frequently the basis for estimating levels of contamination in the intertidal zone. As has been pointed out (Owens 1984b) there exist considerable variations in estimating the level of contamination on gravel beaches. Colour contrasts between oil and the sediments are much greater on sand beaches so that less variability would be expected from those situations.

In the case of gravel beaches the colour of the sediments can vary depending upon the wetness of the surface materials, as was evident during the 1983 survey, and the colour of the surface oil can change considerably through time, for example between the

1983 and 1985 surveys. Visual estimates of surface contamination can provide significantly different values when compared to more detailed and systematic ground observations. These visual estimates are then used to produce numbers to describe the volume of oil remaining on a beach, for example, for estimating a clean-up operation parameters, the importance of such errors becomes evident.

The most simple measure of shoreline contamination is to estimate the length of oiled shoreline. In this instance the length of oiled shoreline is derived from the more detailed surface oil cover observations by measuriing the lengths of the intertidal sections on the surface oil cover maps where the oil cover was greater than 25%. This is considerably more accurate than would be a ground or aerial estimate of the length of oiled shoreline. Although this approach is considerably more sophisticated than would be used in practice it does yield comparitive results for this discussion.

A comparison of changes in the length, area and volume values derived from this study, expressed in terms of the changes from the initial oil, show that the most simple one-dimensional measurement of length produces the least change (Table 5.6). As the degree of sophistication of measurement and estimation increases, and therefore the accuracy increases, the degree of change becomes significantly greater. The surface oil cover data

Table 5.6 Length, Area and Volume Per Cent Changes from Initial Oiling

	Length of Oiled Shoreline (>25% cover)	Total Surface Area Oiled	Estimated Oil Volume
26 Aug 1981	100%	100	100
11 Aug 1982	90	113	65
15 Aug 1983	70	45	28
9 Aug 1985	65	50	33

provide more accurate information than estimates of either (a) the length of contaminated shoreline, or (b) the length and width of the contamination; both of which could be obtained from aerial surveys. These ground surface oil observations involve the additional factor of estimated per cent oil cover to the basic areal data. For example, in this study it is possible to identify the size of the intertidal area which is characterised by the asphalt pavement in 1983 and again in 1985 (325 and 205m^2 respectively). By contrast, a simple two-dimensional measurement of width and length would provide information on the total area of surface oil alone, the addition of a per cent oil cover factor enables the values to be more accurately weighted.

The inclusion of a third dimension to the estimates, the depth of oiled sediments, is enhanced by information by information on the total hydrocarbon contents of the oil-in-sediments by weight. The estimated oil volume for the 1985 data (Table 5.5) gives a value that is in the order of one-third of the initial oil remaining on the beach. By comparison the simple length measurement would indicate that two-thirds of the oil remain on the shoreline (Table 5.6 and Figure 5.7).

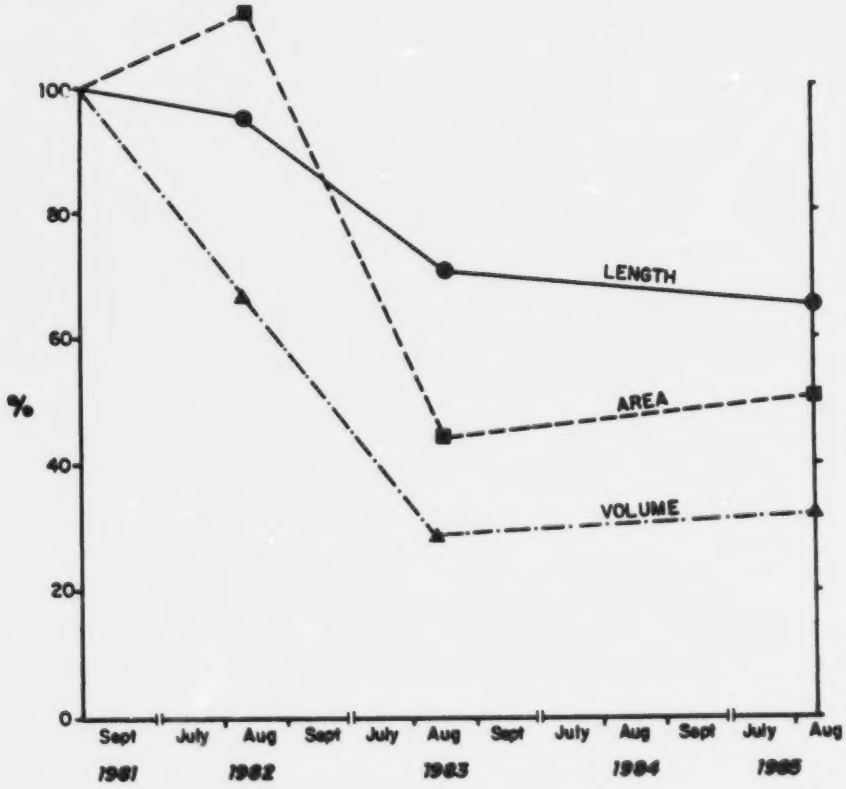


Figure 5.7 Comparison of estimates used to describe the degree of contamination on Bay 11 (from Table 5.6).

5.7 Summary

The Bay 11 investigations represent an attempt to evaluate the short- and long-term fate of crude oil stranded in the intertidal zone. Field observations during the open-water season and the chemical analysis of sediments provide information and data on the changing character of the contaminated shoreline. Initial visual observations showed that considerable amounts of oil remain in the shorezone. The detailed measurements and analyses indicate that relatively little change occurred over the 5 to 6 month open-water preiod between the 1983 and 1985 field studies. The long-term results (1981 to 1985) represent a time period of approximately 12 open-water months: or one year in lower latitude (ice-free) environments.

(a) Total Hydrocarbon Analysis

- overall mean values and individual values from repeat surface and subsurface samples collected in 1985 along profile lines across the intertidal zone had decreased by comparison with previous years' data
- the surface samples continue to show a decrease in concentrations from the upper towards the low intertidal zone
- samples collected within morphologic beach zones show the same patterns as in 1983:

  (1) six additional samples from the asphalt pavement on the beach-face slope had a mean value of 19,000 mg/kg, as compared to a 1983 mean value of 19,800 mg/kg

  (2) a single trough sample from 1985 has a value of 1,700 mg/kg (compared to a mean of three 1983 samples of 500 mg/kg)

  (3) three samples from a ridge in the lower intertidal zone had a 1985 mean of 11,600 mg/kg as compared to two 1983 values of 9,700 and 500 mg/kg

- although there are some evident decreases in the total hydrocarbon concentrations on the repeat samples, there is no significant change in the overall mean value of all samples (1983: 8,150 - 1985: 8,400 mg/kg): this reflects the dominant influence of the asphalt pavement which contains almost half of the remaining stranded oil

(b) Weathering Ratios

- these ratios have been relatively stable since 1982 and the only trend from 1983 to 1985 has been the increase in the number of low values

(c) Surface Oil Cover

- the total surface oiled was unchanged from 1983 to 1985 (1983 - 3,925 versus 1985 - 4,400m^2) and the average surface oil cover was only slightly reduced (from 34 to 27%)

- the primary contamination is on the beach-face where the areal extent of the asphalt pavement decreased from 325 to 205m^2

- the secondary contaminated area is a ridge in the lower intertidal zone, which also decreased slightly in area

(d) Estimated Oil Budget

- using the surface oil cover and the t-h analysis results, calculation of an oil budget indicates that the volume of oil in the surface sediments remained unchanged between 1983 and 1985

- the budget estimates yield more accurate values than estimates of the length and contaminated shoreline or the surface oiled area

- the long-term evaluation indicates that about one-third of initial volume of stranded oil remains in the intertidal zone

6.0 SUMMARY AND CONCLUSIONS

6.1 Z-Lagoon Sites

The 1985 investigations focused only upon the backshore control plots at Crude Oil Point and the backshore control/mixed plots in Bay 106. A few samples were collected at the sites of the 1981 countermeasure experiments and on the low-energy control plots in Bay 103. Following the 1983 project a review of the results indicated that there would be little value in resampling the other sites due either to natural cleaning of the plots or due to dispersion and edge effects.

A significant finding from the 1985 sample analyses is that the mean value of the surface samples collected from the control plots in Bay 106 is similar to that from the Crude Oil Point backshore plots, taking into account the fact that the latter have been subject to physical weathering processes for sixty months as opposed to thirty six months for the Bay 106 plots. The subsurface samples from 1985 taken at both sites produce almost identical mean total hydrocarbon concentration values. The data set from the Crude Oil Point plots shows that there has been a slow but real reduction in surface and subsurface total hydrocarbon concentrations over the five years of study. The mean value for the four surface samples collected in 1985 is 15,750 for the crude plot and 10,675 mg/kg for the emulsion plot: the respective subsurface sediment sample concentrations are 5,450 and 6,225 mg/kg.

The diagnostic weathering ratios show that physical evaporative weathering was initially high (1980 - 1981) for the surface sediments but has since stabilised at a relatively low level. Subsurface samples were collected only during 1985 so it is not possible to define any trends through time, however these results suggest that subsurface physical evaporative weathering rates are slower than those at the surface. The weathering ratio data set for Bay 106 is incomplete but the 1983 and 1985 analyses also suggest that subsurface physical evaporative weathering rates are lower than those at the surface. The biodegradation ratio (ALK/ISO) yields little valuable information for the Crude Oil Point backshore plots but the 1983 and 1985 data from Bay 106 suggest that the biodegradation processes were slower on the mixed as compared to the control plots. This is perhaps the opposite of the expected trend as it was anticipated that the mixing process would expose larger surface areas to degradation processes and therefore increase rates of biological or biochemical weathering. This has apparently not taken place.

Visually all of the backshore plots show a weathering of the surface hydrocarbons to produce a dull, dark-grey colour. Exposure of the subsurface sediments by sample collection shows that these retain a very fresh, unweathered appearance and are both black and shiny. The effect of mixing on the Bay 106 backshore plots was to present a more acceptable surface, in terms of the visual appearance of the hydrocarbons and in terms

of the trafficability of animals or birds across the backshore zone. These mixed plots appear less oiled and as the oil and sediments have been thoroughly mixed there is less likelihood of oil adhering to the feet of anything that crosses the plot.

The countermeasure experiments that involved mixing of the backshore sediments on Bay 106 were designed to replicate oil that might become stranded during periods of elevated water levels above the normal limit of wave action. The results of this experiment show initially (during the first year of observations) that the mixing procedure succeeded in significantly reducing the total hydrocarbon content of the surface sediments. This was offset by a significant increase in the concentrations of total hydrocarbons in the subsurface sediments. In addition the diagnostic weathering ratios showed that the surface sediments had undergone greater evaporative weathering that the subsurface sediments.

These conclusions must now be modified in the light of the 1985 analytical results as the data show that after the third year virtually no difference exists between the mean total hydrocarbon concentrations in the surface and subsurface sediments and between the control and mixed plots. The conclusion that can be drawn from this three-year data set is that the mixing procedure initially accelerated the natural physical weathering processes, but that over the study period the untreated control plots underwent the same processes and achieved the same lowered hydrocarbon concentrations as the mixed plots. The longer term data also indicates, from the diagnostic weathering ratios, that

physical evaporative weathering over this time period was not improved by the mixing procedure, and that the mixing action may have reduced rather than enhanced biodegradation processes.

Some visible oil remains in the intertidal zone at the location of the low-energy control plots in Bay 103, on the crude oil plot only, and also at the location of the test plots on the south shore of Crude Oil Point which were laid down in 1981. In addition some oil remains in the subsurface sediments mixed intertidal plots that were part of the 1981 experiments. The mixing activities on this latter beach buried the surface oil to a depth below that of the wave processes that have acted on this beach between 1981 and 1985.

6.2 Bay 11

6.2.1 Surface Oil Cover

Prior to the detailed observations that were carried out in 1985, visual estimates of the surface oil cover indicated that there had been a considerable reduction as compared to the 1983 photographs and surface oil cover map. These observations were made on a dry and relatively sunny day (see Owens 1984(b)). The measurements of the surface oil cover along repeat profile lines show that this visual estimation was inaccurate and that in fact there had been a small, probably insignificant, increase in the surface oil

cover from 3,925m^2 in 1983 to 4,400m^2 in 1985. This inaccuracy is attributed to the fact that the surface of the oil cover had undergone weathering to produce a more grey tone that was closer in colour to the natural colour of the gravel sediments. The initial length of oiled shoreline, in August 1981, taken from the surface oil cover maps was 275m. This was reduced in 1983 to 190m and only slightly reduced in 1985 to 180m.

The length of oiled shoreline and the area of contamination had apparently stabilised as a result of the formation of an asphalt pavement in the beach-face slope of the upper intertidal zone. The area of the pavement decreased from 1983 to 1985 from 325 to 205m^2. The actual pattern of oil distribution remained constant with a secondary area of oil on the surface of a ridge in the lower part of the intertidal zone. This oil distribution pattern reflects in part the morphology and sediments of this particular beach and also the higher degree of physical (mechanical) weathering in the lower half of the intertidal zone.

An important aspect of the surface oil cover data is that it reflects not only the two-dimensional aspects of oil on the sediment surface but that it includes a density factor. The observations made along the profiles were an estimate of the per cent oil cover at each point. It is possible therefore

to obtain an average of the surface oil cover through time. Although the total oiled area actually increased slightly in 1983 to 1985 the average surface oil cover decreased from 34% to 27% over the same time period.

6.2.2 Oil Budget Estimates

Estimates of the volume of oil remaining in the intertidal zone can be calculated using the surface cover data from the repeated ground observations and from total hydrocarbon concentration values derived from analysis of surface sediments. The mean of the repeat samples collected from the upper, middle and intertidal zones is 2,600 mg/kg, but the mean of a total of twenty three samples collected from Bay 11 produces a value of 8,400 mg/kg: this compares to a mean of 8,150 mg/kg from the nineteen samples that were collected in 1983. These concentrations suggest that both the area and the concentration of surface oils was relatively stable between 1983 and 1985. It is not surprising therefore that the oil budget estimates have not changed significantly between the two dates.

The surface area of the asphalt pavement decreased from approximately 325 to 205m^2 between 1983 and 1985, although the hydrocarbon concentration values remained constant. As a result the estimated volume of oil contained within the pavement was reduced from 0.7 to 0.45m^3. Visual obser-

vations confirm this general trend as the pavement appeared softer and also thinner in 1985 as compared to 1983. This reduction of oil contained within the pavement and its spread to adjacent areas, which have lower oil concentrations, is substantiated by the small increase in the total surface oil cover.

Over the first 6 open-water months of this study (1981 to 1983) the estimated volume of oil on the intertidal zone was reduced from between 7 and $8m^3$ to approximately $2m^3$. Over the second 6 open-water months (1983 to 1985), there has been no major change in either the surface area of contamination or the volume of oil remaining in the intertidal zone. It is likely that the oil that remains will exist for an extended time period as it is in a stable form, either within the asphalt pavement or as a coating of individual pebbles or as clumps of pebbles in an oil matrix. A further data set from this study site in summer 1987 would likely yield valuable information for the third 6-month period on the history of the fate of the oil stranded on this sheltered beach.

The data from Bay 11 represent approximately 12 months of open-water conditions in a very sheltered marine environment. The results can be applied to lower latitude (ice-free) environments.

6.3 Geochemical Data

6.3.1 Saturated Hydrocarbon Weathering Ratio (SHWR)

This ratio is derived from the sum of the n-alkanes from n-C10 to n-C25, divided by the sum of the n-alkanes from n-C17 to n-C25. The resulting figure indicates the loss, by evaporation, of the low boiling saturated hydrocarbons (n-C10 to n-C17). As this loss increases so the ratio approaches 1.0.

The fifteen surface samples collected in 1985 from Bay 11 produce a mean SHWR of 1.27: with seven samples having a value of 1.0 and 11 samples having a ration less than 1.25. The results over the entire sampling period from Bay 11 (Table 5.5(a)) would indicate that by the time of the survey in 1982 most of the stranded intertidal oil had lost all of the low boiling saturated hydrocarbons by evaporative weathering.

The mean of the 1985 surface samples from the backshore T and IM plots is 1.56 and that of the subsurface samples is 1.99 (Table 6.1). As shown in Figure 6.1 it must be remembered that the samples were taken from oils spilled or laid down over three summer seasons. When viewed in the long term context it appears not surprisingly that the ratios from intertidal samples were reduced more rapidly and remained lower than the ratios of backshore samples.

Table 6.1 Summary of 1985 Geochemical Ratios (mean values)

	SHWR	ALK/ISO	AWR	n
(a) intertidal surface samples				
Bay 11 and L1/L2	1.25	0.95	1.73	17
(b) supra-tidal (T1/T2: IMC/IME)				
surface samples	1.56	2.01	1.78	6
subsurface samples	1.99	2.10	2.05	6

Table 6.2 AWR Ratios - All Sites 1985

	CRUDE (L1-T1-IMC-Bay 11)	EMULSION (L2-T2-IME)
n	20	3
surface	1.8	2.75
n	4	3
subsurface	2.25	3.22

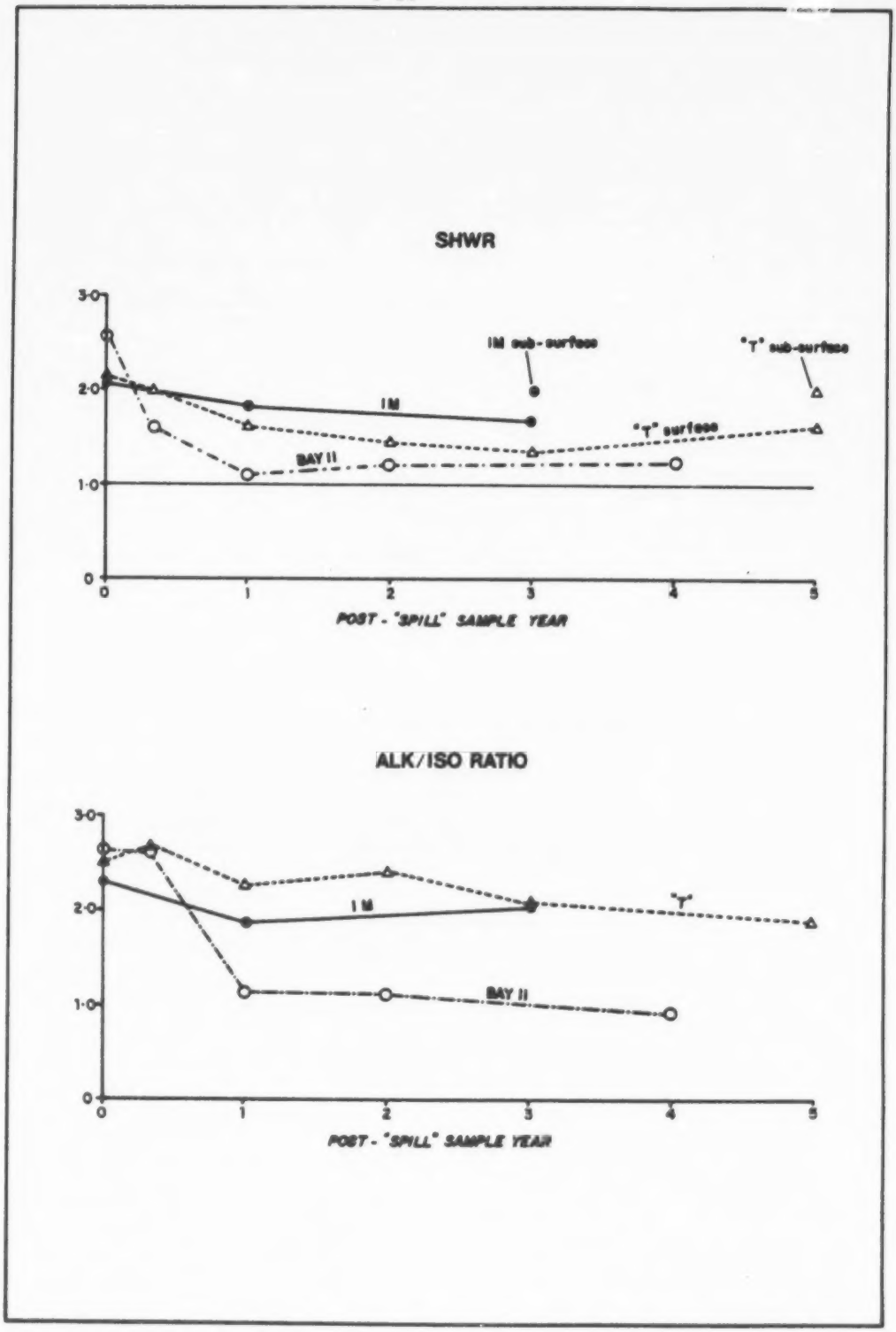


Figure 6.1 Mean values of weathering ratios through time (IM data is from control plots only).

6.3.2 Alkane/Isoprenoid Ratio (ALK/ISO)

This ratio is derived from:

$$ALK/ISO_{14-18} = \frac{1400 + 1500 + 1600 + 1700 + 1800}{1380 + 1470 + 1650 + 1708 + 1810}$$

(i.e. the numerator is the C14 to C18 alkanes with the denominator being the five isoprenoids in the n-C13 boiling range).

The ratio provides an index of biodegradation. As the n-alkanes are preferentially depleted the ratio approaches zero.

The fifteen surface samples collected from Bay 11 in 1985 have a mean value of 0.95 (Table 5.5(b)), which compares to the combined backshore surface sample mean of 2.01 (Table 6.1). Only four of the Bay 11 surface samples have a ratio greater than 1.5. The results over the entire sampling period (Table 6.1 and Figure 6.1) show a relatively rapid rate of biodegradation between the stranding of the oil in 1981 and the next sample collection in August 1982, since which there has been little change.

Comparison with the backshore sites (Table 6.1) shows consistently lower ratios on the intertidal versus the backshore plots.

6.3.3 Aromatic Weathering Ratio (AWR)

This value is obtained from the following formula:

$$AWR = \frac{\text{Akyl benzenes + naphthalenes + fluorenes + phenanthrenes + dibenzothiophenes}}{\text{Total phenanthrenes + dibenzothiophenes}}$$

As the low boiling aromatics are lost by physical evaporation and/or dissolution this ratio approaches 1.0. Prior to the 1985 survey relatively few AWR values were defined and there are no complete data sets for any one site so that no long-term trends can be defined.

Data is available only from the 1985 samples and these are summarised in Table 6.2 for the intertidal versus supratidal samples. An interesting difference appears if all of the crude samples are compared to the emulsion plots (Table 6.2). From this one set of data it appears that the degree if aromatic weathering is much greater on the crude oil plots. This may be due to the fact that the aromatics are only removed more slowly from the emulsion as the physiochemical properties of the oil only allow the low boiling point aromatics to escape at slower rates.

6.4 Conclusions

The results of the 1985 field and analytical programme just summarised in Section 6.0 show clearly that the 1985 follow-on project yielded valuable information to evaluate the long-term fate of oil stranded in the intertidal zone on a sheltered gravel beach and also on the backshore, above the limit of normal wave action. There exists a consistency between data sets that is encouraging, for example between the backshore plots at Crude Oil Point and in Bay 106.

The original BIOS shoreline study involved the detailed consideration of specific sites often over short-term periods. The study has now evolved into one which is considering longer term patterns and trends. Less emphasis is placed on individual values but rather on trends in both time and space. Over the period of studies to date it is evident that the major changes took place following the initial stranding or distribution of oil onto the shoreline. In some cases considerable fluctuations in the data sets occurred during the first and second open-water seasons but during the third, and where applicable, fourth and fifth, open-water seasons the contaminated oils became more stabilised. This stability is most evident and most significant on Bay 11 where the oil in the upper intertidal zone formed an asphalt pavement which has remained, and will likely remain for a long time, as a resilient feature.

The only countermeasure experiment that has extended into the 1985 study is that of the backshore mixing plots that was conducted in Bay 106 in 1982. The interesting long-term trend that is evident is that the mixing activity initially resulted in considerable differences when compared to the control plots, but that after a period of approximately 9 open-water months the hydrocarbon concentrations and the diagnostic weathering ratios indicate that little difference exists between the mixed and control plots. The mixing activity initially accelerated the physical weathering processes but over that time period the same end result was achieved on the non-mixed plots.

One aspect of the project to date has been to use the field observations and data to identify levels of accuracy for estimating degrees of contamination in the event of real-world spills. Although estimates of the length of contaminated shoreline are the easiest set of information to obtain, frequently on the basis of aerial surveys, the results would most likely be an over-estimate of the actual degree of contamination. The calculated oil budget estimates for the Bay 11 area yielded information which suggests that from 1981 to 1985 the total volume of stranded oil remaining is only one-third of the initial oiling. By contrast the information obtained on the length of oiled shoreline indicated that in 1985 two-thirds of the study beach remained oiled. As always, greater accuracy involves more detailed and therefore more expensive studies.

Nevertheless these estimates of contamination are very important when operational decisions are made on the basis of volumes of contaminated oil that are required to be removed from the shore-zone.

The backshore control plots on Bay 106 and on Crude Oil Point show that the volumes of total hydrocarbons are slowly decreasing by natural processes in this cold climate environment. The results from the intertidal zone surveys on Bay 11 extend over an equivalent open-water season of approximately 12 months. The data that have evolved from this study to date can be used in lower latitudes (ice-free environments) and can be compared with data from real or experimental spills outside of the immediate study area.

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APPENDIX A: TOTAL HYDROCARBON BY INFRARED

A1: METHODOLOGY

Extraction Procedure. Between 0.5 and 2.0 kg of beach sediment were placed in a Teflon extraction jug with a Teflon lid. About 0.2 kg of Freon 113 was added and the sample shaken on a paint shaker for 5 minutes. If the extract showed visible oil content, a 4 mL aliquot was transferred to a small break-neck ampoule which was then sealed in a flame. If there was no visible oil in the extract, two 20 mL aliquoits were transferred to two large break-neck ampoules. The weight of each aliquot was recorded.

When very highly oiled samples were extracted, some dark precipitate remained in the extraction jug. This was not the case when CCl_4 was used. This material was soluble in CCl_4. A solution of this material in CCl_4, which was opaque to visible light, was analysed in the same manner as the extracts. No CH_2 absorption at 2850^1 cm was observed. As the analytical method is based on this CH_2 absorption it was felt that the change to Freon 113 would not bias the results relative to the CCl_4 extraction method.

Infra-red Analysis. The analysis of oil by Infra-red absorption is based on the CH_2 absorption at 2850^1 cm. A calibration curve based on the absorpiton of Lagomedio standard solution was used to determine the concentration of the sample.

Sample extracts that were visibly very concentrated were diluted gravimetrically before analysis. Samples that were visibly dilute were concentrated by gentle evaporation with a stream of dry nitrogen before analysis.

The extracts were analysed on a Perkin-Elmer 337 Infra-red Spectrometer. This instrument has adjustable slits and scan speeds.

Daily calibrations were done using seven standard Lagomedio crude solutions in Freon 113. The concentrations of the standards varied from 100 mg/kg to 2000 mg/kg. The corresponding peak heights varied from 12 mm to 102 mm. The standard error of the absorption of the standards over 21 days of analysis was 1 mm at all concentrations. A second order regression curve was determined each day. The sample concentrations were calculated from this curve.

Based on a 15x concentration of dilute extracts, the detection limit is 30 mg/kg (0.003%), defined as a signal height three times the width of the noise, with a precision of 10 mg/kg (0.001%). At higher concentrations, the precision of the analysis is 1% of value, based on the measurement precision of the absorption.

TOTAL HYDROCARBONS BY IR: RESULTS

SAMPLE NUMBER	BAY	DESCRIPTION	TYPE	[OIL] mg/kg
5001	11	Profile 2 Upper Surface	TH	1200
5002	11	Profile 2 Upper Subsurface	TH	54
5003	11	Profile 2 Middle Surface	TH	147
5004	11	Profile 2 Middle Subsurface	TH	54
5005	11	Profile 2 Lower Surface	TH	1600
5006	11	Profile 2 Lower Subsurface	TH	3200
5007	11	Profile 4 Upper Surface	TH	6100
5008	11	Profile 4 Upper Subsurface	TH	180
5009	11	Profile 4 Middle Surface	TH	2500
5010	11	Profile 4 Middle Subsurface	TH	820
5011	11	Profile 4 Lower Surface	TH	47
5012	11	Profile 4 Lower Subsurface	TH	11
5013	11	Profile 6 Upper Surface	TH	4600
5014	11	Profile 6 Upper Subsurface	TH	140
5015	11	Profile 6 Middle Surface	TH	1300
5016	11	Profile 6 Middle Subsurface	TH	300
5017	11	Profile 6 Lower Surface	TH	280
5018	11	Profile 6 Lower Subsurface	TH	39
5019	11	Profile 8 Upper Surface	TH	9500
5020	11	Profile 8 Upper Subsurface	TH	19
5021	11	Profile 8 Middle Surface	TH	3700
5022	11	Profile 8 Middle Subsurface	TH	2700
5023	11	Profile 8 Lower Surface	TH	120
5024	11	Profile 8 Lower Subsurface	TH	56
5025	11	X1, WC Pr. 11 Surface	TH	12700
5026	11	X2, WC Pr. 5+ Surface	TH	26800
5027	11	X3, WC Pr. 5+ Subsurface	TH	360
5028	11	X4, Creek edge Surface	TH	11900
5029	11	X5, Creek edge, 3-8 cm	TH	13000
5030	11	X6, Creek edge, 8-15 cm	TH	16100
5031	11	X7, WC 9, Upper Surface	TH	13900
5032	11	X8, WC 10, Upper Surface	TH	17300
5033	11	X9, WC 11, Upper Surface	TH	25000
5034	11	X10, WC 12, Upper Surface	TH	18100
5035	11	X11, WC 13, MiddleSurface	TH	1700
5036	11	X12, WC 11, Lower Surface	TH	6400
5037	11	X13, WC 10, Lower Surface	TH	3900
5038	11	X14, WC 8, Lower Surface	TH	24400
5044	103	L1, Upper left Surface	TH	1900

SAMPLE NUMBER	BAY			DESCRIPTION	TYPE	[OIL] mg/kg
5075	106	IMC-C	Berm	Surface	TH	47000
5076	106	IMC-C	Berm	Subsurface	TH	9700
5077	106	IMC-C	Back	Surface	TH	12500
5078	106	IMC-C	Back	Subsurface	TH	60
5079	106	IMC-M	Berm	Surface	TH	25900
5080	106	IMC-M	Berm	Subsurface	TH	6200
5081	106	IMC-M	Back	Surface	TH	12500
5082	106	IMC-M	Back	Subsurface	TH	1800
5083	106	IME-C	Berm	Surface	TH	11300
5084	106	IME-C	Berm	Subsurface	TH	12300
5085	106	IME-C	Back	Surface	TH	11800
5086	106	IME-C	Back	Subsurface	TH	37
5087	106	IME-M	Berm	Surface	TH	24200
5088	106	IME-M	Berm	Subsurface	TH	9400
5089	106	IME-M	Back	Surface	TH	15300
5090	106	IME-M	Back	Subsurface	TH	7300
5091	106	ITZ-1		Surface	TH	21
5092	106	ITZ-2		Surface	TH	16
5093	106	ITZ-3		Surface	TH	43
5094	106	ITZ-4		Surface	TH	140
5095	106	ITZ-5		Surface	TH	43
5096	106	ITZ-6		Surface	TH	89
5097	106	ITZ-7		Surface	TH	300
5098	106	ITZ-8		Surface	TH	93
5099	103	L1	Upper	Surface	TH	620
5100	103	L1	Upper	Subsurface	TH	3600
5101	103	L1	Middle	Surface	TH	17
5102	103	L1	Middle	Subsurface	TH	110
5103	103	L1	Lower	Surface	TH	29
5104	103	L1	Lower	Subsurface	TH	270
5105	103	L2	Middle	Surface	TH	11
5106	103	L2	Middle	Subsurface	TH	20
5107		1981	CC	Surface	TH	19
5108		1981	CC	Subsurface	TH	73
5109		1981	MC	Surface	TH	470
5110		1981	MC	Subsurface	TH	8000
5111		1981	CE	Surface	TH	19
5112		1981	CE	Subsurface	TH	69
5113		1981	ME	Surface	TH	31
5114		1981	ME	Subsurface	TH	1500
5115		1981	D(E)E	Surface	TH	9
5116		1981	D(E)E	Subsurface	TH	59

SAMPLE NUMBER	BAY			DESCRIPTION	TYPE	[OIL] mg/kg
5117		1980	T1-1	Surface	TH	15700
5118		1980	T1-1	Subsurface	TH	4900
5119		1980	T1-2	Surface	TH	12800
5120		1980	T1-2	Subsurface	TH	1100
5121		1980	T1-3	Surface	TH	19900
5122		1980	T1-3	Subsurface	TH	11100
5123		1980	T1-4	Surface	TH	14600
5124		1980	T1-4	Subsurface	TH	4700
5125		1980	T2-1	Surface	TH	5200
5126		1980	T2-1	Subsurface	TH	4900
5127		1980	T2-2	Surface	TH	7200
5128		1980	T2-2	Subsurface	TH	12600
5129		1980	T2-3	Surface	TH	18500
5130		1980	T2-3	Subsurface	TH	3300
5131		1980	T2-4	Surface	TH	11800
5132		1980	T2-4	Subsurface	TH	4100

APPENDIX B. GAS CHROMATOGRAPHY

B.1 METHODOLOGY

Compositional Sediment Extraction. Samples were extracted by a base digestion method based upon that of Cretney et al. 1980.

Sediment samples were taken from storage at -20° C and allowed to thaw for analysis. A subsample of the thawed sediment (50-80 g) was weighed into a 500 mL round bottom flask, to which was added 100 mL of methanol and 5 g of potassium hydroxide.

The sample was refluxed gently for one hour, allowed to cool for 5 minutes then 100 mL of pre-extracted distilled water added, and refluxed for a further 30 minutes. The extract was allowed to cool and decanted into a 1-L separatory funnel and the sediment residue rinsed with 2 x 25 mL methanol and 100 mL pentane. The washings were transferred to the separatory funnel which was shaken vigorously for 1 minute to partition the hydrocarbons into the pentane. After settling, the aqueous layer was drawn off into a second separatory funnel and extracted with another 2 x 100 mL pentane. The pentane extracts were combined and washed with 3 x 150 mL solvent extracted distilled water, dried 5 minutes over anhydrous sodium sulphate in a 500 mL Erlenmeyer and taken down to 5-10 mL by vacuum rotary evaporation at 30 ° C, and then to 100 mL by nitrogen jet evaporation in a centrifuge tube.

Samples were fractionated into non-polar (f-1) and polar (f-2, aromatic) fractions.

Extract fractionation. The method reported in Boehm et al. (1984) was followed. Fractionation columns consist of 11 g 100% activated silica gel, 1 g 5% deactivated alumina, and 1 g copper. The columns were prepared by eluting with dichloromethane, then hexane. The sample hexane extract was placed on the column and eluted first with hexane, to elute the non-polar fraction (f-1), and then with dichloromethane/hexane (1/1) to elute the polar fraction (f-2). The eluates were reduced in volume for subsequent GC/FID or GC/MS analysis.

GC/FID analysis. GC/FID analytical techniques and conditions are the same as those reported in Part 2 of this report.

GC/MS analysis. GC/MS analytical techniques and conditions are the same as those reported in Part 2 of this report.

REFERENCES

Boehm, P., W. Steinhauer, D. Cobb, S. Duffy and J. Brown. 1984. Chemistry 2: Analytical Biogeochemistry - 1983 Study Results. Baffin Island Oil Spill Working Report 83-2; 139 p. Environmental Protection Service, Environment Canada, Ottawa.

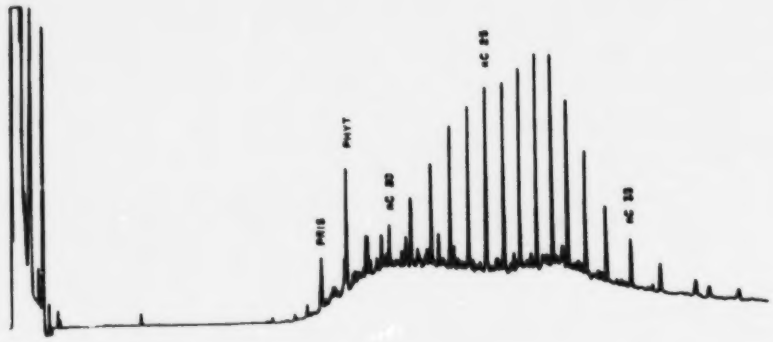
Cretney, W.J., C.S. Wong, P.A. Christensen, B.W. McIntyre and B.R. Fowler. 1980. Quantification of polycyclic aromatic hydrocarbons in marine environmental samples. In: Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment. Ed. by B.K. Afaghan and D. McKay, Environmental Science Research Series. Plenum Press, New York.

WEATHERING INDICES
COUNTERMEASURE EXPERIMENT SEDIMENTS

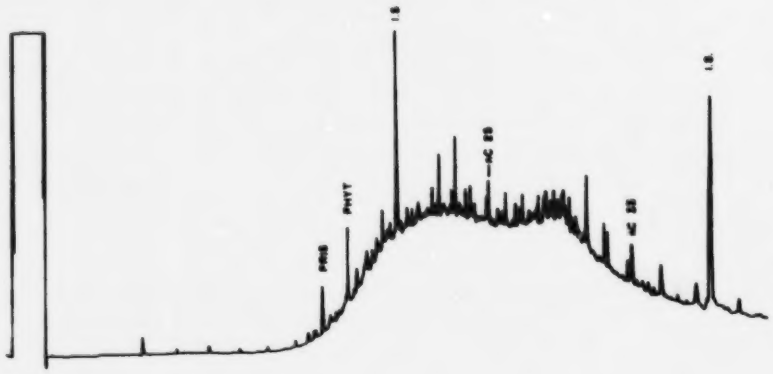
ID	SAMPLE	SHWR	ALK ISO	C18 PHYT	PRIS PHYT	CPI	AWR	[OIL] (IR) mg/kg	OIL? (Subjective)
5133	1980, T1, Surface	1.6	2.0	1.8	0.7	1.5	1.8	16000	+
5134	1980, T1, Subsurface	1.9	2.1	1.5	0.6	1.2	1.9	5500	+
5135	1980, T2, Surface	1.1	1.8	1.5	0.6	1.3	1.3	11000	+
5136	1980, T2, Subsurface	2.2	2.3	1.8	0.8	1.3	2.7	6200	+
5143	1980, L1, Surface	1.0	0.2	0.2	0.4	1.3	1.1	620	+
5144	1980, L1, Subsurface	1.2	0.5	0.4	0.8	1.4	1.5	3600	+
5145	1980, L2, Surface	1.2	3.6	2.9	1.3	3.2	4.8	11	
5146	1980, L2, Subsurface	1.5	2.3	2.4	3.6	5.8	2.7	20	-
5070	1980, L1 Upper Subsurface	1.8	1.6	0.9	0.7	1.3	1.7	1900	+
5137	1981, CC, Surface	1.4	2.1	1.6	1.0	1.4	2.8	19	+
5138	1981, CC, Subsurface	1.5	1.8	1.1	0.8	1.3	2.1	73	+
5139	1981, CE, Surface	1.4	1.1	0.5	0.6	1.5	2.0	470	+
5140	1981, CE, Subsurface	1.8	2.1	1.5	0.8	1.3	2.8	8000	+
5141	1981, MC, Surface	1.3	1.4	0.8	0.7	1.1	1.5	69	+
5142	1981, MC, Subsurface	1.3	0.3	0.2	0.7	1.3	1.8	1500	+
5147	1982, IMC-C Surface	1.6	1.7	1.3	0.7	1.3	1.5	30000	+
5148	1982, IMC-C Subsurface	1.5	1.5	1.0	0.7	2.1	1.9	4900	+
5149	1982, IMC-M Surface	1.8	2.0	1.4	0.7	1.3	3.0	19000	+
5150	1982, IMC-M Subsurface	1.8	2.0	1.6	0.8	1.4	2.3	4000	+
5151	1982, IME-C Surface	1.6	2.3	1.5	0.7	1.3	2.6	12000	+
5152	1982, IME-C Subsurface	2.3	2.4	1.6	0.7	1.3	3.7	6200	+
5153	1982, IME-M Surface	1.6	2.4	1.6	0.7	1.3	2.3	20000	+
5154	1982, IME-M Subsurface	2.3	2.4	1.5	0.7	1.3	3.8	8400	+

WEATHERING INDICES
BAY 11 SHORELINE SEDIMENTS

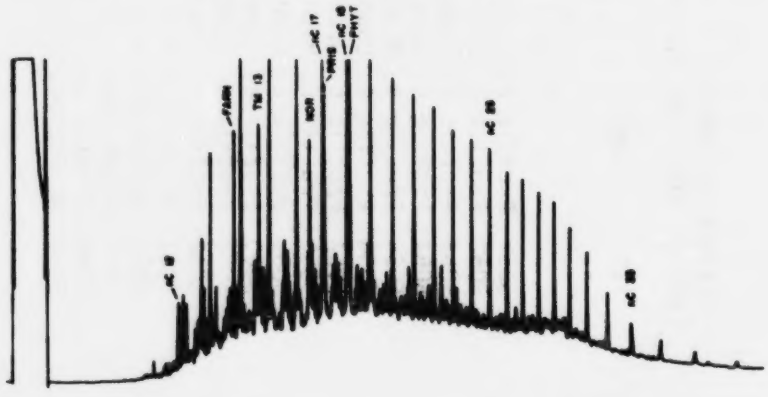
ID	SAMPLE	SHWR	ALK ISO	C18 PHYT	PRIS PHYT	CPI	AWR	[OIL] (IR) mg/kg	OIL? (Subjective)
5051	Profile 2, Upper Surface	1.0	0.4	0.4	0.4	1.4	1.1	1200	+
5052	Profile 2, Middle Surface	1.0	0.1	0.2	0.4	1.2	1.7	150	+
5053	Profile 2, Lower Surface	1.7	1.4	0.8	0.6	1.3	2.3	1600	+
5054	Profile 4, Upper Surface	2.4	2.4	1.6	0.7	1.3	3.4	6100	+
5055	Profile 4, Middle Surface	1.0	0.1	0.1	0.4	1.2	1.1	2500	+
5056	Profile 4, Lower Surface	1.4	1.5	0.8	0.6	1.1	3.5	47	+
5057	Profile 6, Upper Surface	1.0	0.2	0.1	0.5	1.2	1.2	4600	+
5058	Profile 6, Middle Surface	1.0	0.1	0.2	0.4	1.2	1.1	1300	+
5059	Profile 6, Lower Surface	1.0	0.5	0.8	0.5	N/A	1.8	280	+
5060	Profile 8, Upper Surface	1.3	1.6	1.1	0.5	1.3	1.9	9500	+
5061	Profile 8, Middle Surface	N/A	0	0	0.6	N/A	1.5	3700	+
5062	Profile 8, Lower Surface	1.0	0.4	0.4	0.5	1.0	1.2	120	+
5063	WC Profile 11, Surface	1.2	0.4	0.3	0.7	1.3	1.4	13000	+
5064	WC Profile 5+, Surface	1.6	2.2	1.4	0.6	1.3	2.5	27000	+
5065	Creek Edge, Surface	1.2	1.7	1.3	0.6	0.7	1.5	12000	+
5066	Creek Edge, 3-8 cm	1.8	2.0	1.6	0.8	1.3	2.4	13000	+
5068	WC Profile 10, LowerSurface	1.3	1.2	0.7	0.6	1.3	1.4	3900	+



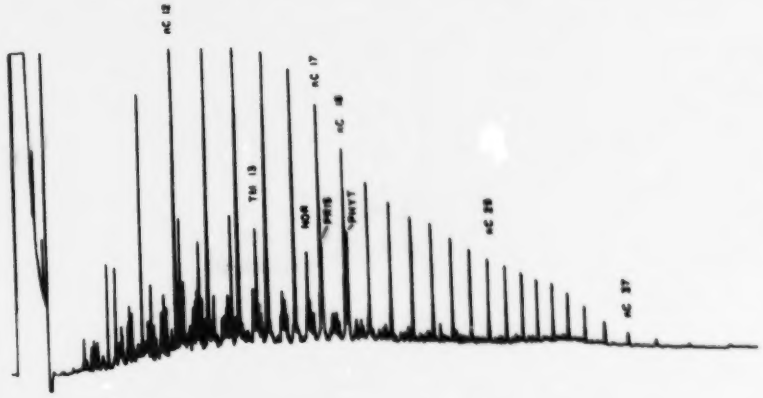
5051: Bay 11, Profile 2 Upper Surface



5052: Bay 11, Profile 2 Middle Surface

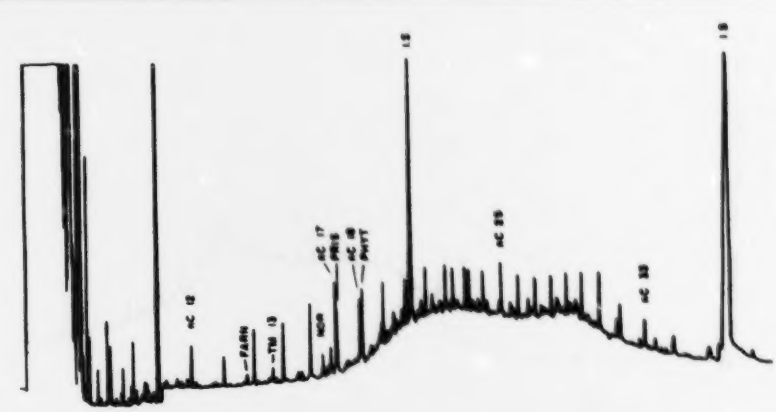


5053: Bay 11, Profile 2 Lower Surface

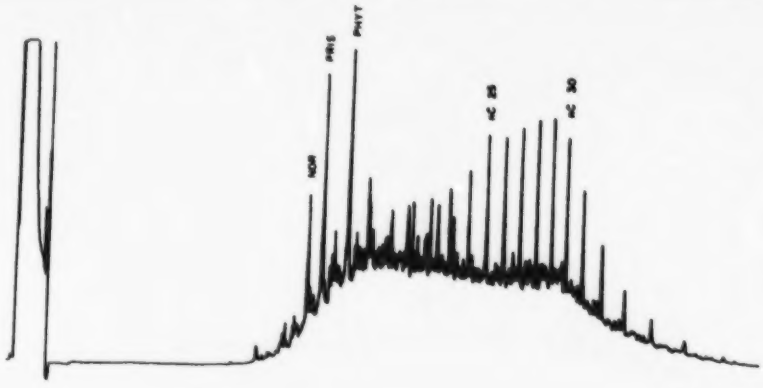


5054: Bay 11, Profile 4 Upper Surface

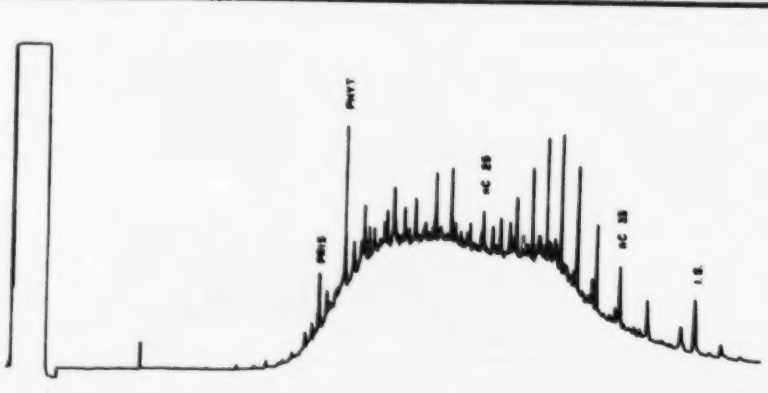
5055: Bay 11, Profile 4 Middle Surface



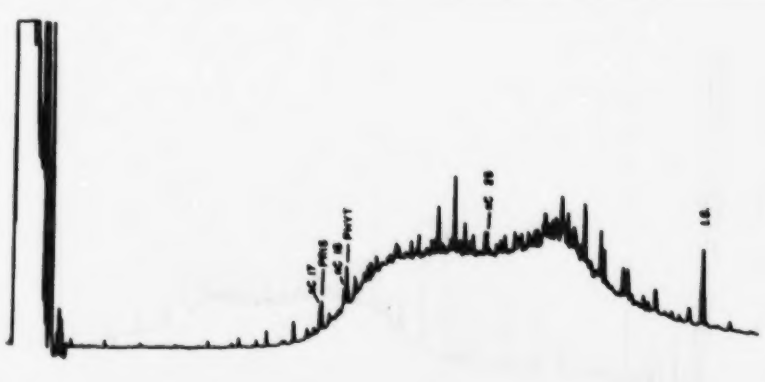
5056: Bay 11, Profile 4 Lower Surface



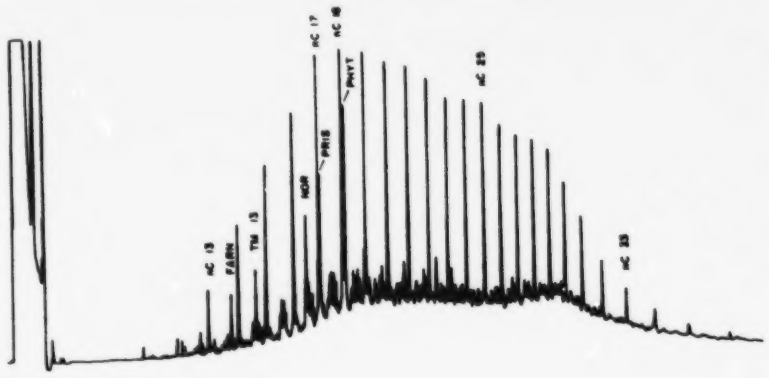
5057: Bay 11, Profile 6 Upper Surface



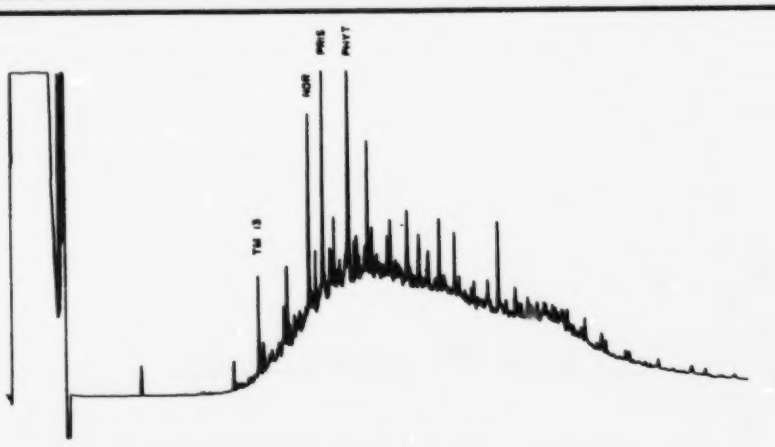
5058: Bay 11, Profile 6 Middle Surface



5059: Bay 11, Profile 6 Lower Surface



5060: Bay 11, Profile 8 Upper Surface



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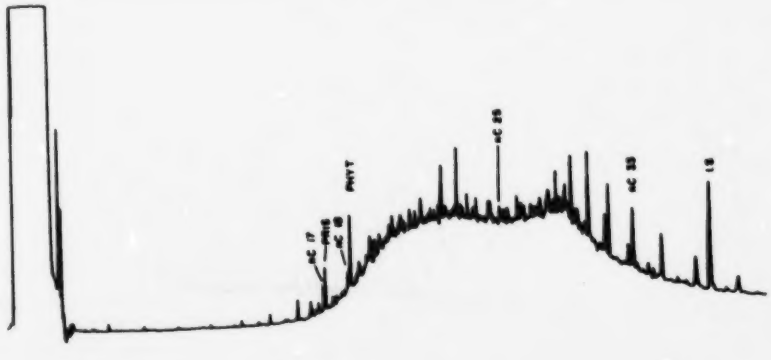
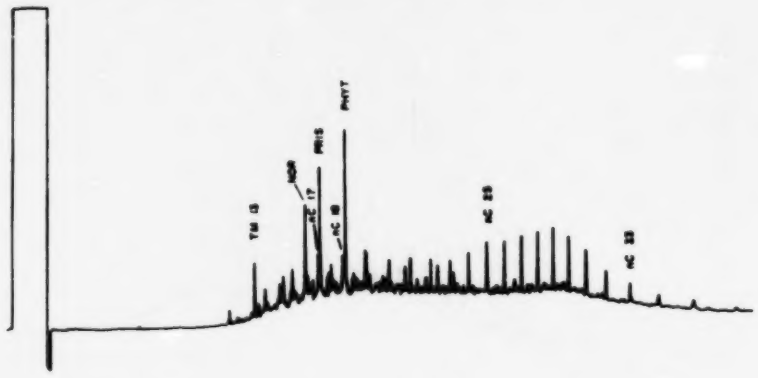
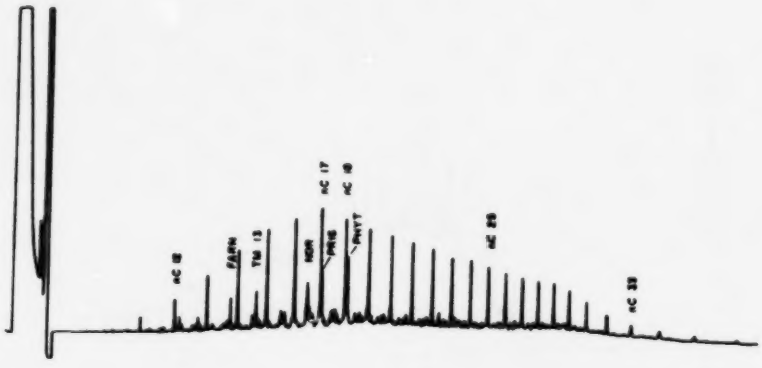


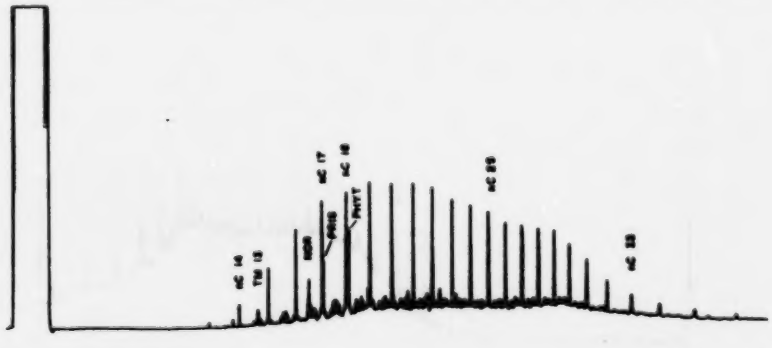
5062: Bay 11, Profile 8 Lower Surface



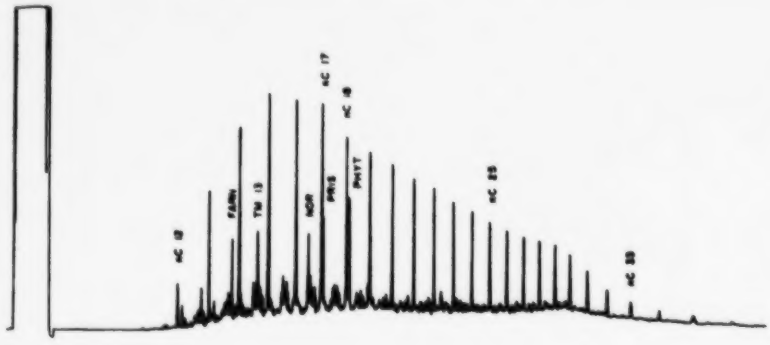
5063: Bay 11, MC 11 Surface



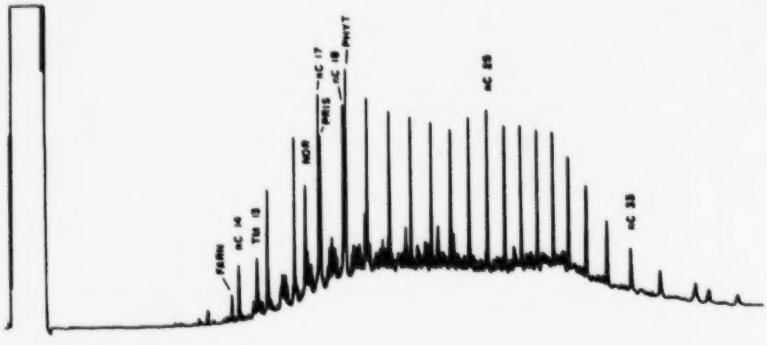
5064: Bay 11, MC 5+ Surface



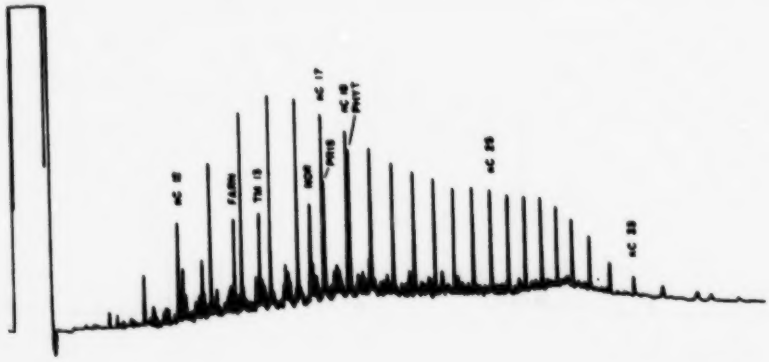
5065: Bay 11, Creek Edge Surface



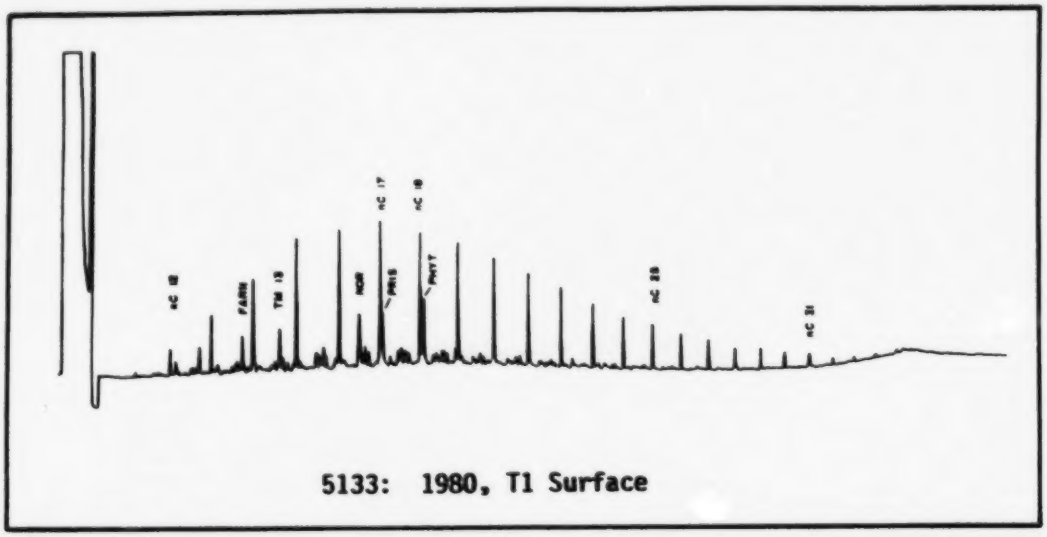
5066: Bay 11, Creek Edge, 3-8 cm



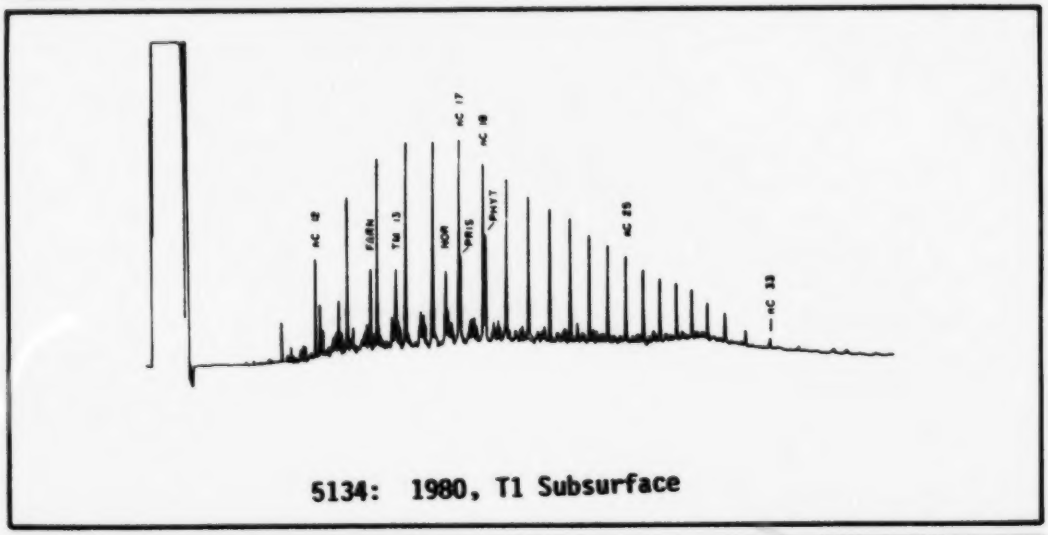
5068: Bay 11, MC 10 Lower Surface



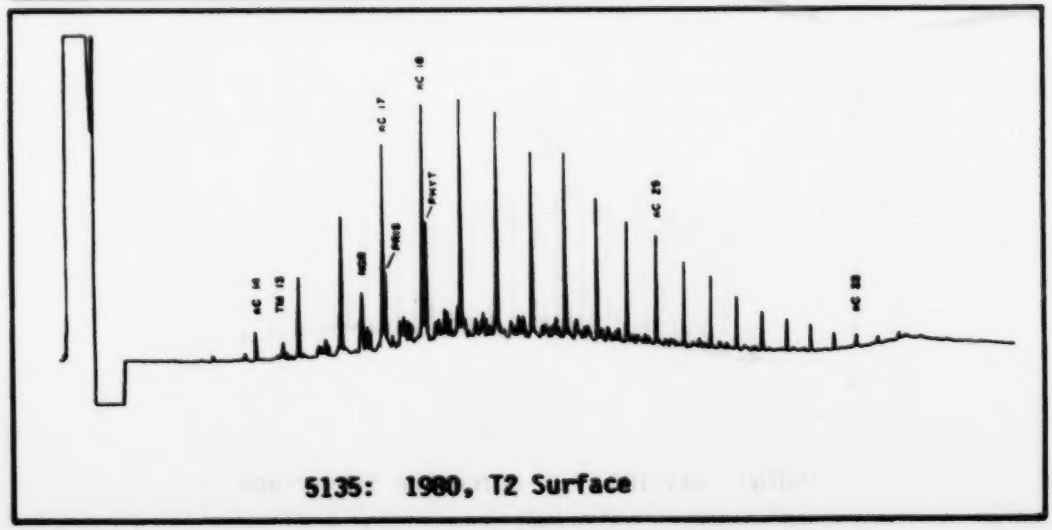
5070: Bay 103, 11 Up/Centre Subsurface



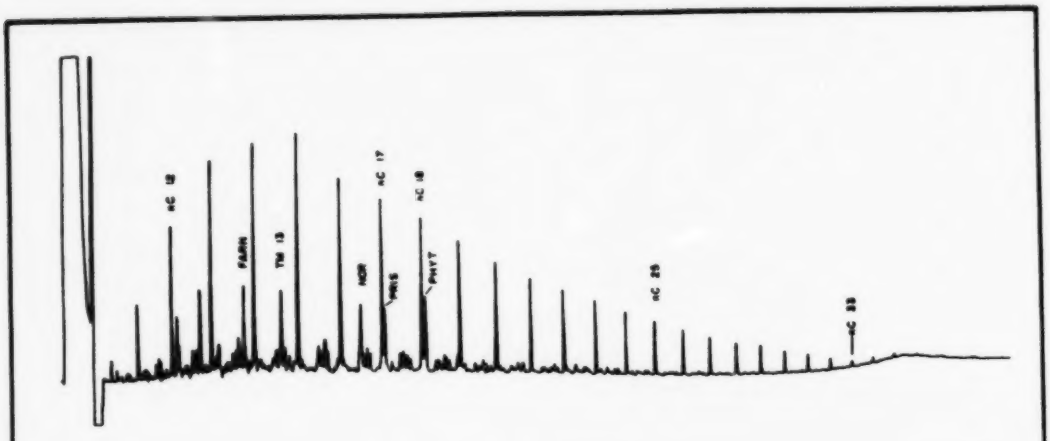
5133: 1980, T1 Surface



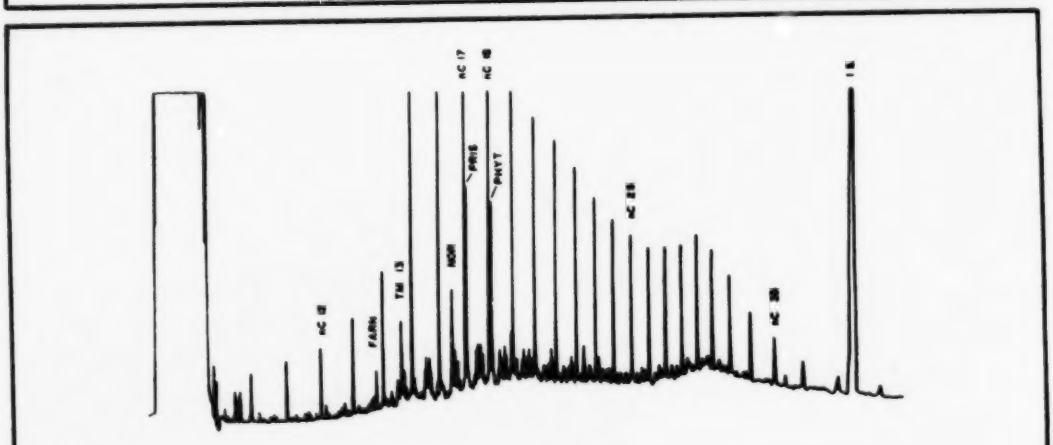
5134: 1980, T1 Subsurface



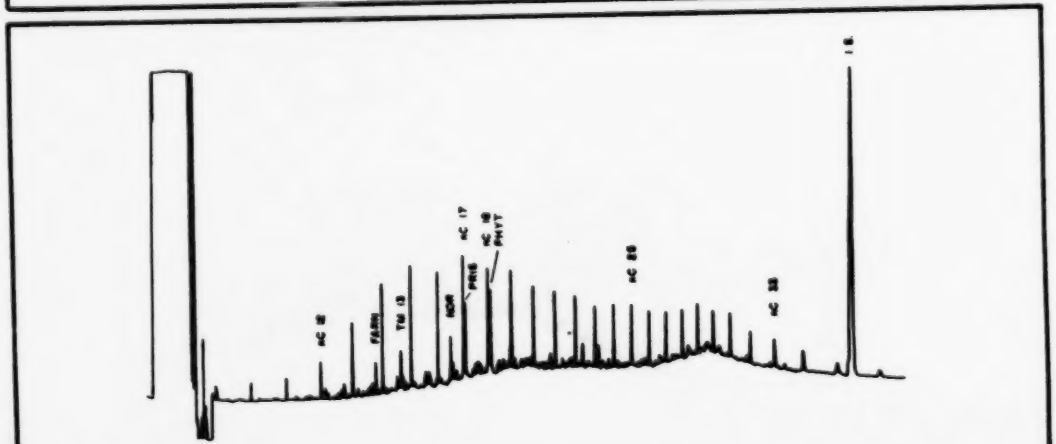
5135: 1980, T2 Surface



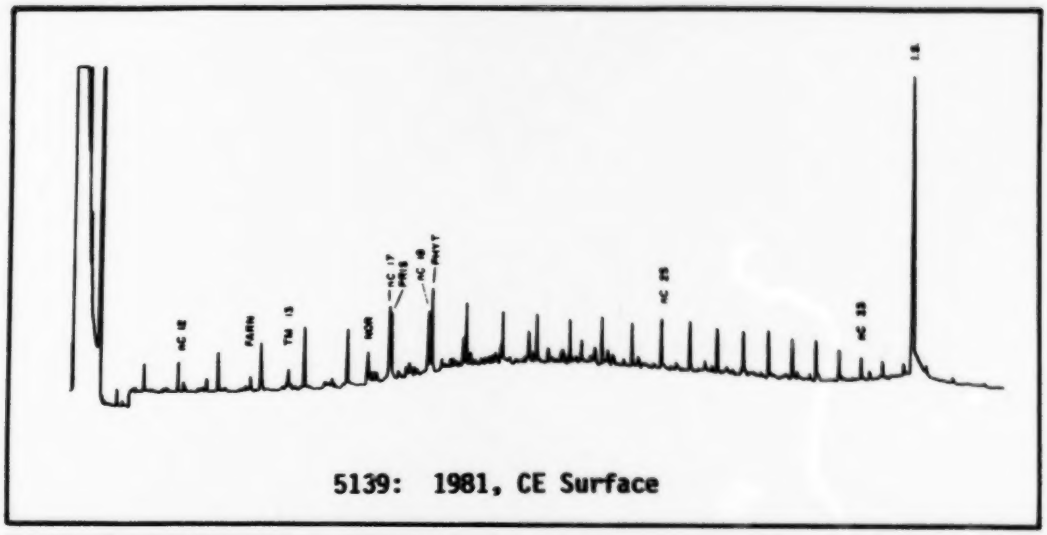
5136: 1980, T2 Subsurface



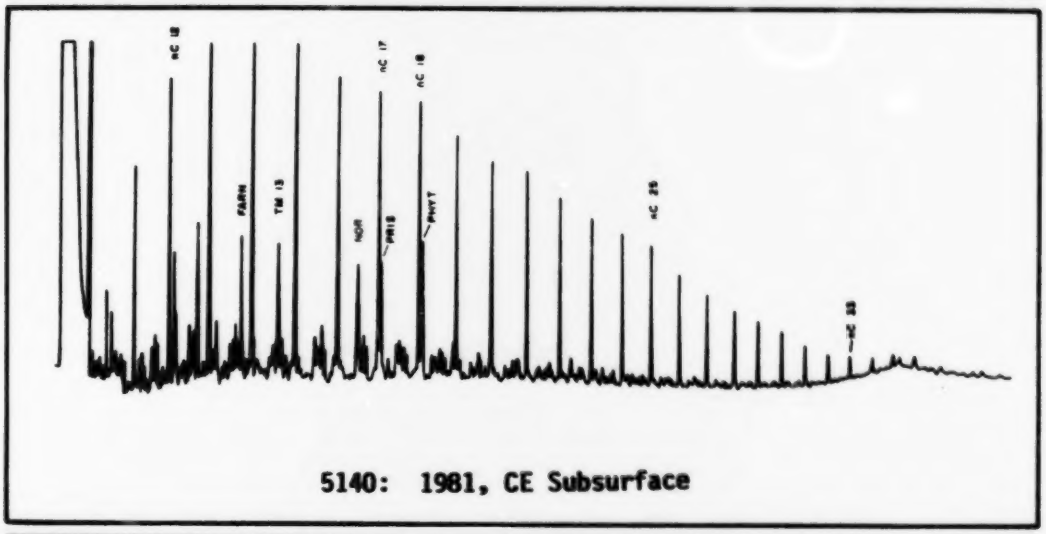
5137: 1981, CC Surface



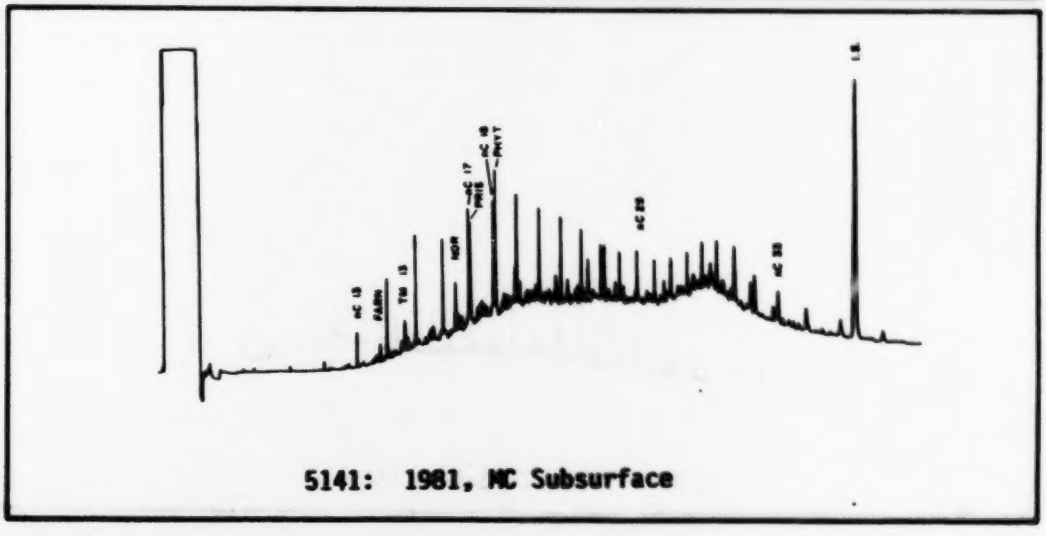
5138: 1981, CC Subsurface



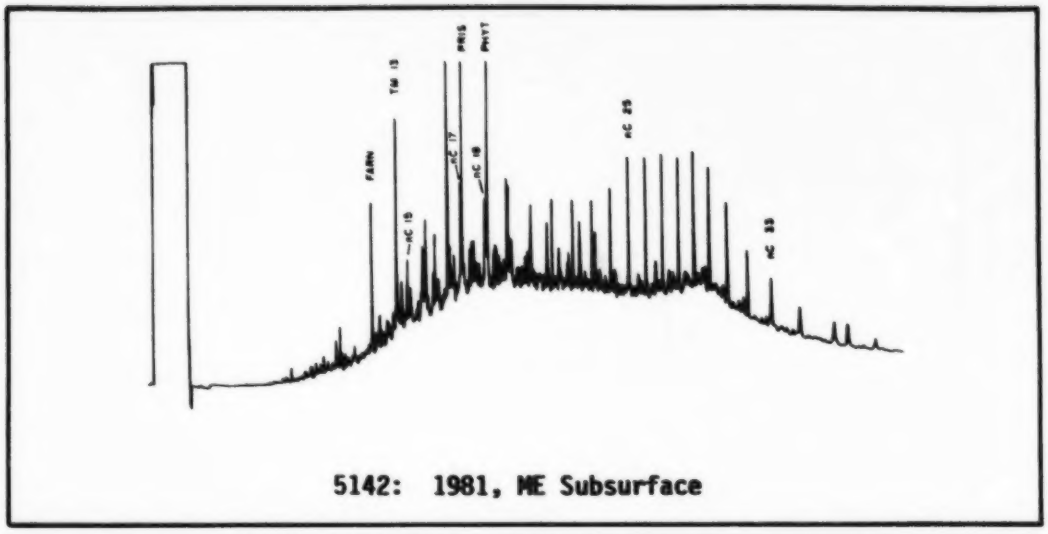
5139: 1981, CE Surface



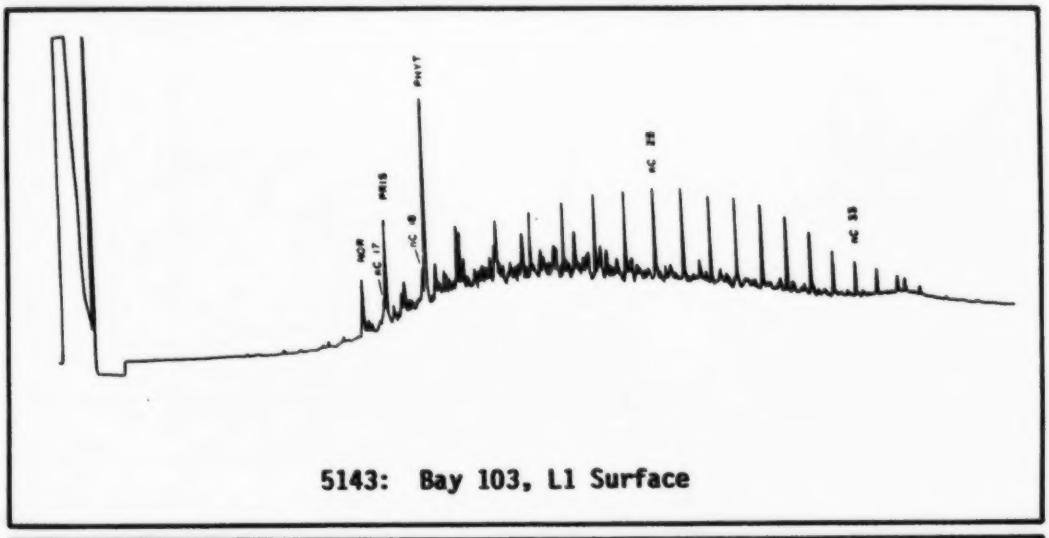
5140: 1981, CE Subsurface



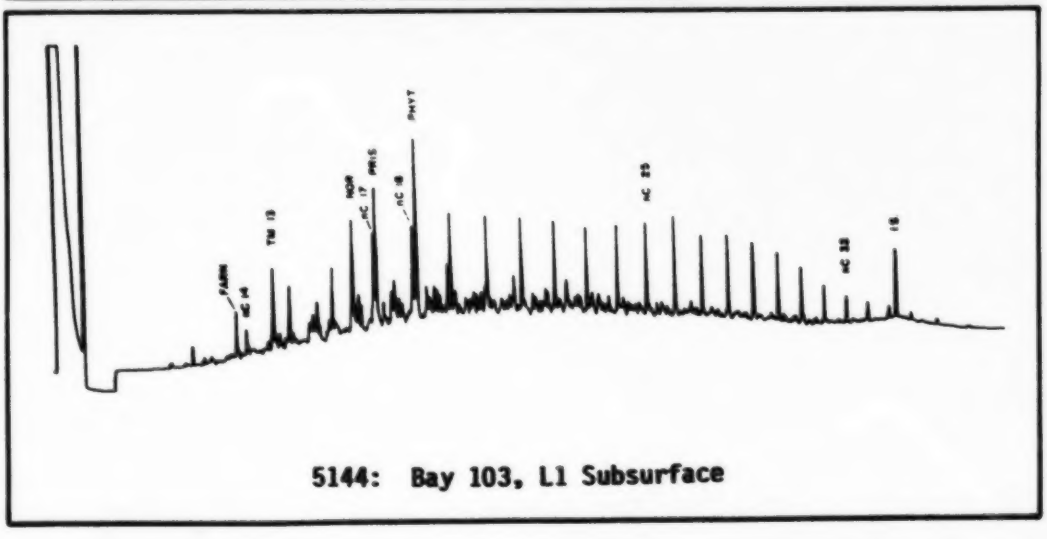
5141: 1981, MC Subsurface



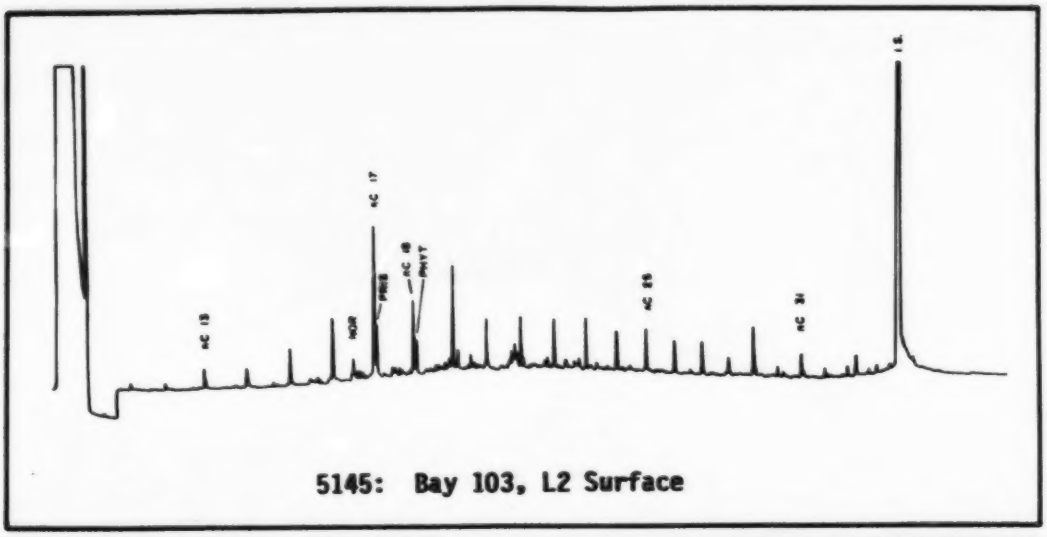
5142: 1981, ME Subsurface



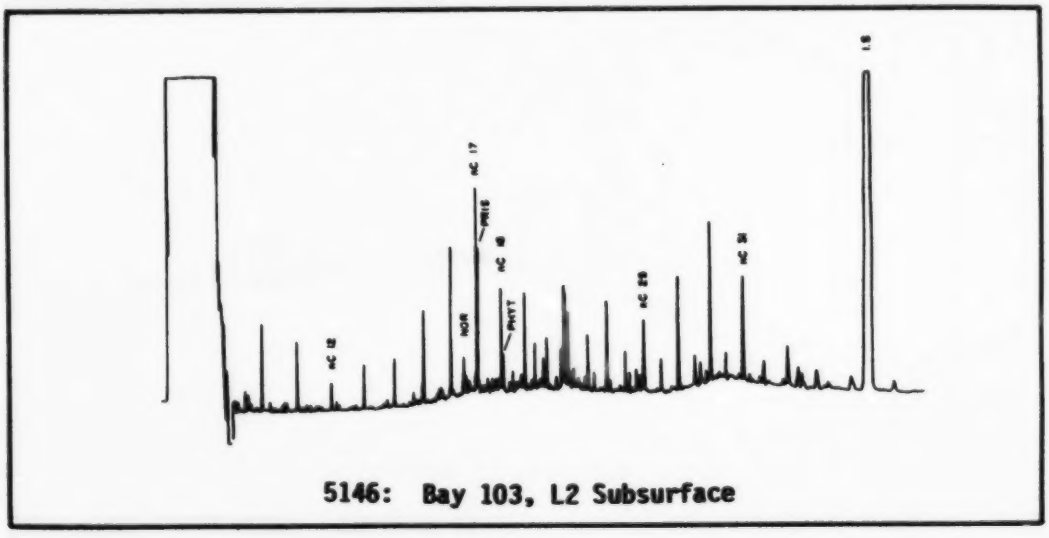
5143: Bay 103, L1 Surface



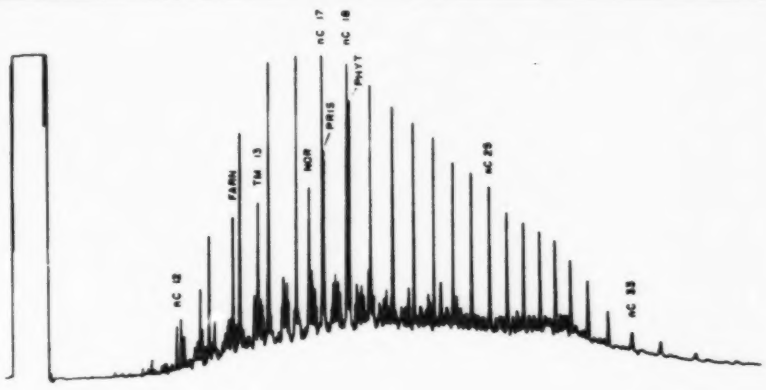
5144: Bay 103, L1 Subsurface



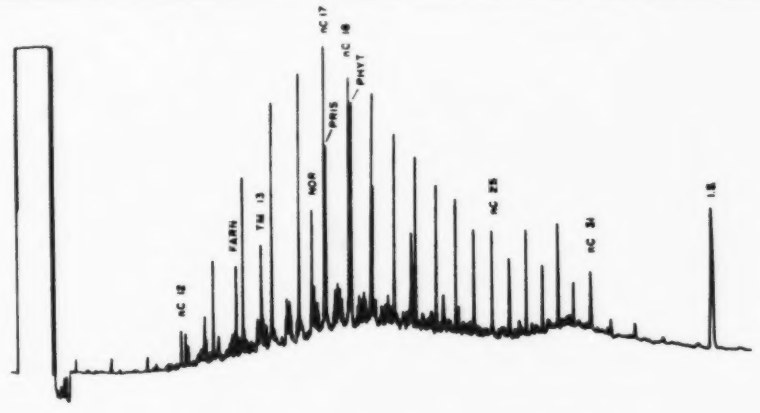
5145: Bay 103, L2 Surface



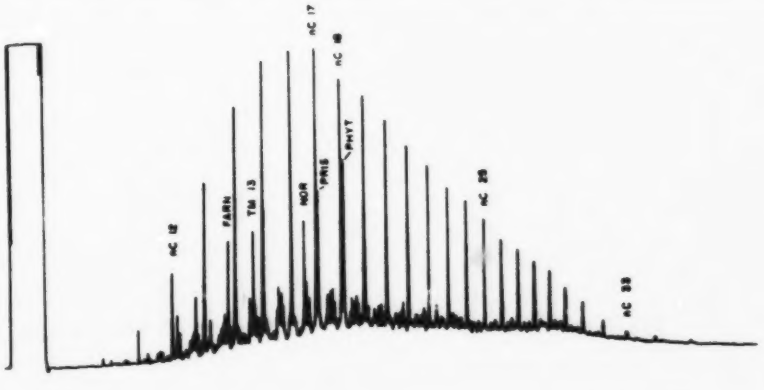
5146: Bay 103, L2 Subsurface



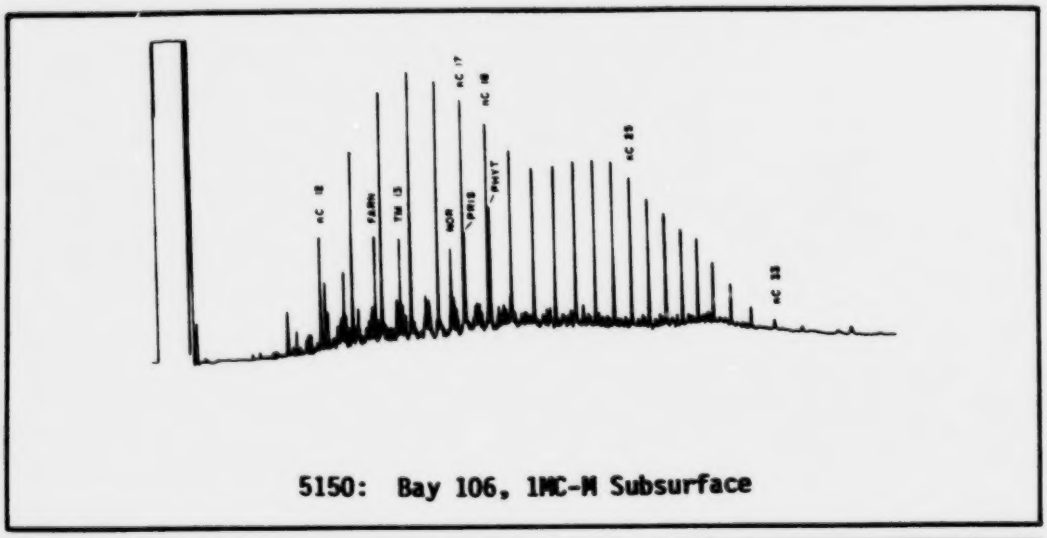
5147: Bay 106, 1MC-C Surface



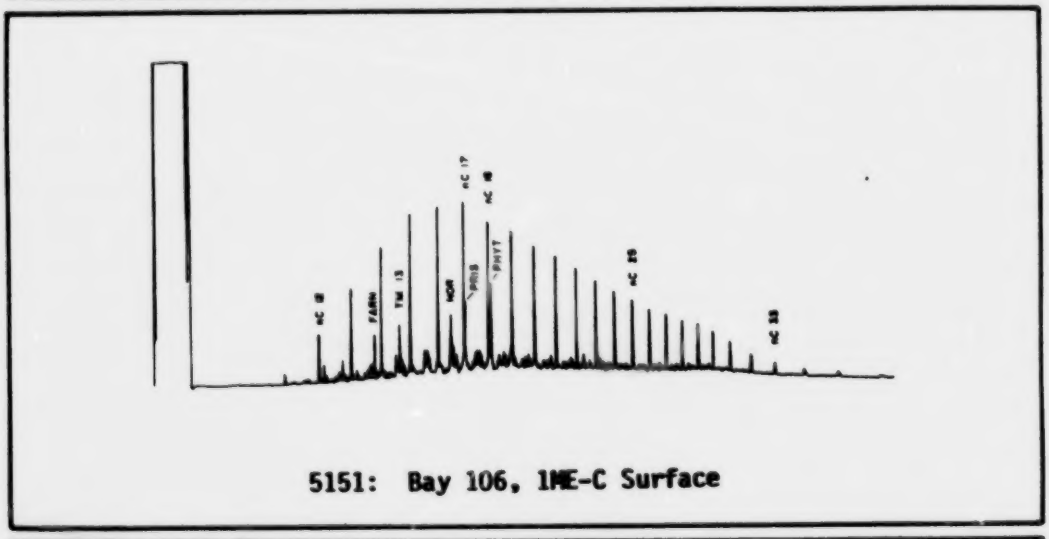
5148: Bay 106, 1MC-C Subsurface



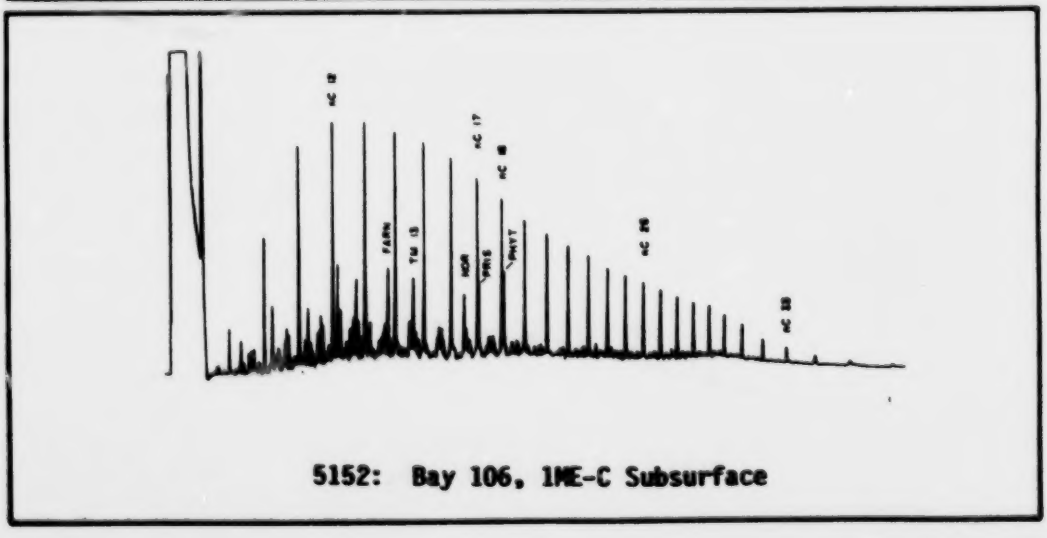
5149: Bay 106, 1MC-M Surface



5150: Bay 106, 1MC-M Subsurface



5151: Bay 106, 1ME-C Surface



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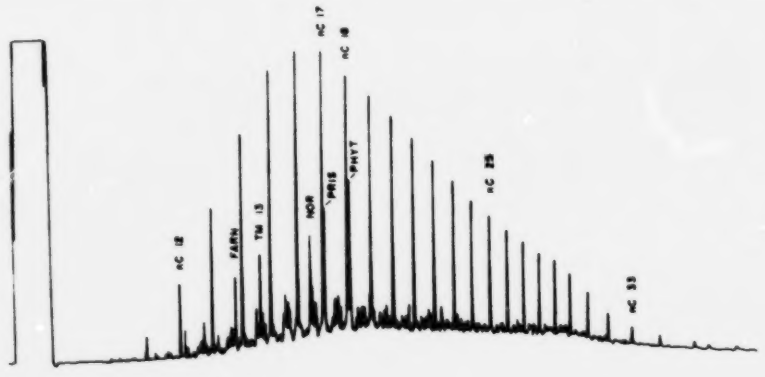

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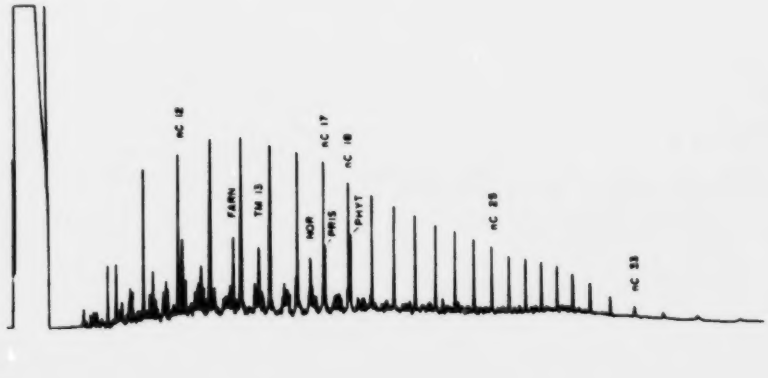


5154: Bay 106, 1ME-M Subsurface

LONG TERM FATE AND PERSISTENCE OF STRANDED OIL AT CAPE HATT, N.W.T. AND FROM THE AMOCO CADIZ SPILL

Part 2: Cape Hatt Sub-tidal Sediments

D. Hope
B. Humphrey
Seakem Oceanography Ltd.

TABLE OF CONTENTS

		Page
8.	INTRODUCTION	8/9-1
9.	METHODOLOGY	
	9.1 Sampling	8/9-1
	9.2 Analysis	9-3
10.	RESULTS	
	10.1 Bay 11	10-1
	10.2 Bay 9	10-1
11.	DISCUSSION	11-1
12.	REFERENCES	12-1
APPENDIX C: Gas Chromatography		C-1
APPENDIX D: Data Summaries		
	D1: Alkane Data	D-2
	D2: PAH Data	D-4

8. INTRODUCTION

The introduction of petroleum hydrocarbons into the sub-tidal area adjacent to the oiled beach in Bay 11 was predicted during the planning of the BIOS project, and the results of the analyses of the biology transects at 3 and 7 m in 1982 prompted a sampling and analysis program to determine the extent and concentrations of hydrocarbon off the beach. The results (Boehm et al., 1984) indicated a relationship between distance offshore and hydrocarbon concentration. In 1985, the same stations were sampled, with two additional profiles extending into the bay. These samples were analysed by synchronous scan ultra-violet fluorescence (UV/F), gas chromatography with flame ionization detection (GC/FID), and gas chromatography with mass spectrum detection (GC/MS).

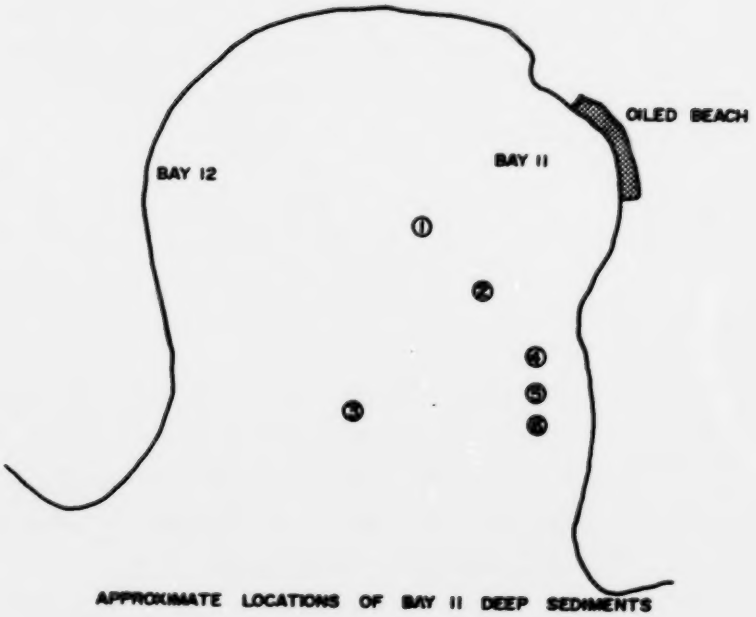
9. METHODOLOGY

9.1 Sampling

Sediment samples for hydrocarbon analysis were collected by divers using 250 mL wide-mouth glass jars. Closed jars were transported to the bottom, lids were removed, and the top 2 cm of sediment was collected by gently scraping the jar along the substrate. The jars were closed and returned to the surface. A Teflon liner was placed under the lid and the sample was frozen until analysis.

The deep sediment were collected from locations offshore from the oiled Bay 11 beach, in areas expected to contain sediment which may have been transported from the beach. The locations are indicated in Figure 9.1. The profile sediments were collected along lines extending out from the oiled beach. The profile sampled in 1983 is identified as Profile 1 (Bunch), indicating the line connecting the south transect with the south microbiology station. A line 75 m south of Profile 1 and a line 75 m north of Profile 1, extending from near the center of the oiled beach, are Profiles 2 and 3 respectively. Divers collected samples at regular intervals along the profiles. The locations of the profile samples are indicated in Figure 11.1. Bay 9 samples were collected along the line of the diffuser pipe and 5 m north of that line, at 5 m and 10 m depths.

Figure 9.1



APPROXIMATE LOCATIONS OF BAY 11 DEEP SEDIMENTS

9.2 Analysis

Extraction of sediment samples. Sediment samples for hydrocarbon analysis were collected in baked glass jars with FEP (hydrocarbon clean) liners and kept frozen until extraction.

Approximately 100 g of wet sediment was placed in a glass jar and water removed with three 75 mL rinses of methanol. Internal standards were added and the sediment extracted with 3 x 100 mL dichloromethane/hexane (9/1) by shaking on a platform shaker for four hours per extract. All extracts (methanol and dichloromethane/hexane) were placed in a separatory funnel with 100 mL water, and pH was adjusted to 2 with HCl. The dichloromethane layer was removed. Three additional extractions with 100 mL of dichloromethane were performed and the extracts combined, reduced in volume, and the solvent displaced with methanol. The methanol extract was digested with 4 mL of 10 N aqueous KOH (80°C water bath)for four hours, then extracted with 3 x 15 mL hexane. The combined hexane extracts were reduced in volume.

Prior to UV/F analysis, the extracts were eluted through an alumina column in order to remove interfering polar and biogenic compounds. The extracts were applied to a 6.5 g column of 7.5% deactivated alumina and eluted with 25 mL of hexane/dichloromethane (9/1). The eluate volume was reduced to 2 mL.

After UV/F analysis, selected samples were fractionated into polar and non-polar hydrocarbons and subsequently analysed by GC/MS or GC/FID.

UV/F Analysis. UV/Fluoroscence spectroscopy (UV/F) is a useful technique for the detection of petroleum contamination in the environment. The fluorescence of petroleum emanates mainly from its aromatic components which are also less subject to weathering and more toxic than the aliphatic compoments. However, the UV/F technique detects any fluorescing compounds which are extracted by the solvent used for analysis.

The attractive features of UV/F for monitoring petroleum hydrocarbons in sediments are its speed, sensitivity and simplicity. The main disadvantage of UV/F in quantitative analysis is the necessity of calibrating the UV/F response with a standard of similar composition to the oil being analyzed.

A conventional fluorescence spectrum consists of a plot of fluorescence intensity as a function of emission wavelength while the sample is radiated with

Table 9.1
GC/FID Analytical Conditions

Column:	25 m x 0.25 mm BP5 5% phenyl, polydimethyl-siloxane bonded phase fused silica column (S.G.E.)
Carrier Gas:	hydrogen
Column Flow Rate:	1.5 mL min-1 (90 cm.s-1 linear rate)
Injector Flow Rate:	60 mL min-1
Injector Pressure:	18 psi
Injector Temperature:	250° C
Detector Temperature:	300° C
Detector Make-Up:	30 mL min-1 nitrogen
Split Ratio:	40:1 (approx.)
Temperature Program:	50° C for 1 min, then 10 C° min-1 to 300° C, and hold for 10 minutes

All injections made in the splitless mode, and stream splitting resumed after 1.0 minute.

Table 9.2
Limit of Detection for Selected Alkanes

Alkane	Detection Limit (ng/sample)
nC12	10
nC16	10
nC20	15
nC28	20
nC36	30

Table 9.3
Abbreviations and Definitions of Terminology

Alk	alkane
Iso	isoprenoid
Farn	farnesane, an isoprenoid
TM13	trimethyltridecane, an isoprenoid
Nor	norpristane, an isoprenoid
Pris	pristane, an isoprenoid
Phyt	phytane, an isoprenoid
PAH	Polycyclic Aromatic Hydrocarbons
AB	alkylbenzenes (C_3 to C_6)
Naph	naphthalene
Fluor	fluorene
Dbt	dibenzothiophene
Phen	phenanthrene
Anth	anthracene
C-0	no alkyl groups
C-1	methyl
C-2	dimethyl or ethyl
C-3	trimethyl, ethylmethyl, isopropyl, propyl
C-4 to C-6	alkylation patterns from 4 to 6 carbons
I.S.	internal standard

UV/light of constant wavelength. Under these conditions complex hydrocarbon mixtures, such as petroleum and its products, produce broad structureless spectra, making it difficult to distinguish between oils of similar aromatic composition. Lloyd (1971a, b, c) has shown that the use of synchronous scan UV/F (SS UV/F) can result in improved resolution in complex mixtures. In this technique the excitation and emission wavelengths are varied simultaneously. Although the fluorescence spectrum of a single species is independent of excitation wavelength, the excitation efficiency of a given component of a mixture of fluorescent compounds will vary with excitation wavelength. Thus the use of a series of excitation wavelengths results in additional discrimination between complex aromatic mixtures. The SS UV/F technique is therefore very useful for distinguishing between different oils (e.g., John and Soutar 1976) and has also been advocated for the determination of petroleum hydrocarbon concentrations in enviornmental samples (e.g., Wakeham 1977).

As in quantitative analysis by conventional UV/F spectroscopy, the SS UV/F response must be calibrated using standard solutions of similar composition. Usually the source oil is used and the results reported as "source oil equivalents". Thus total oil concentations are not actually measured but are inferred. Several sources of error can result from the assumption that the fluorescence in samples is quantitatively related to that from a standard oil (Hargrave and Phillips 1975). These include: (1) the presence of other compounds which fluoresce at similar wavelengths to those of the aromatic compounds present in the oil; and (ii) the UV/F detection of only the aromatic components which comprise a fraction (10 to 60% by weight) of the various oils, and this fraction changes during weathering and degradation. The relative importance of these sources of error will be dependent on the situation being studied.

The results presented below suggest that the UV/F technique produces high results for highly weathered oil in sediments as a result of the monitoring of the more persistent aromatic components. In addition, non-petroleum compounds may contribute to the sample fluorescence and cause high values for oil concentrations.

The method used by Boehm et al. (1984) was followed except that we used a Perkin-Elmer MFP 66 microcomputer controlled spectrofluorometer. The intensity of fluorescence was measured using an excitation wavelength of 325.5 nm and an emission wavelength of 350.5 nm. This corresponds to the peak maximum of Lagomedio Bay 11 reference oil under synchronous scan conditions ($\Delta\lambda$ = 25 nm). Fluorescence intensities were converted to oil concentrations by interpolating from a standard plot of fluorescence intensity versus Lagomedio oil concentration. A set of

standards was prepared from a solution of Lagomedio crude oil which had been eluted through an alumina column in the same way as the sample extracts had been eluted. This was done as a consequence of experiments which showed a loss of sensitivity for uncolumned oil.

Extract fractionation. The method reported in Boehm et al. (1984) was followed. Fractionation columns consist of 11 g 100% activated silica gel, 1 g 5% deactivated alumina, and 1 g copper. The columns were prepared by eluting with dichloromethane, then hexane. The sample hexane extract was placed on the column and eluted first with hexane, to elute the non-polar fraction (f-1), and then with dichloromethane/hexane (1/1) to elute the polar fraction (f-2). The eluates were reduced in volume for subsequent GC/FID or GC/MS analysis.

GC/FID analysis. GC/FID analysis was used to quantify the n-alkanes and isoprenoids present. The visual picture of a GC/FID trace, together with several indicator ratios, was used to determine the presence of oil and how weathered that oil was.

The nonpolar fraction (f-1) of each sample was analysed by capillary gas chromatography on a Hewlett-Packard 5840A gas chromatograph, equipped with a splitless injection port and flame ionization detector. Instrumental conditions are listed in Table 9.1. Compounds were identified by comparing retention indices with that of a known standard. Concentrations were calculated by comparing the integrated areas of peaks with the area of the internal standard (perdeuterated hexatriacontane). Finally, the wet weight:dry weight ratio was used to convert concentrations from a wet weight extraction to a dry weight basis. Limits of detection for selected alkanes are given in Table 9.2 and explantion of abbreviations in Table 9.3.

Several diagnostic ratios (Table 9.4) were calculated from the data. These ratios were used to determine if the sample was biogenic or petrogenic or a combination of both. Typical values of these ratios for Lagomedio fresh and aged oil are given in Table 9.5.

Table 9.4
Diagnostic Ratios

1. Alkane/Isoprenoid Ratio (Biodegradation)

$$\text{Alk/Iso} = \frac{nC14 + nC15 + nC16 + nC17 + nC18}{\text{FARN} + \text{TM13} + \text{NOR} + \text{PRIS} + \text{PHYT}}$$

This ratio approaches 0 as the n-alkanes are preferentially depleted.

2. n-C18/Phytane Ratio

This ratio approaches 0 as n-C18 is preferentially depleted. This is a specific case of the Alk/Iso ratio.

3. Pristane/Phytane Ratio

Pristane occurs commonly in biota and in recent sediments as a degradation product of the phytol side chain of plant pigment chlorophyll whereas phytane is not formed and is not commonly found in recent sediments; consequently, non-petrolum derived hydrocarbons generally give rise to a high pristane/phytane ratio. The pristane/phytane ratio has been used as an indicator of the presence or absence of petroleum. Although a high pristane/phytane ratio is generally a reliable indicator of the absence of petroleum, the converse is not necessarily true, that is, low values are less reliable indicators of the presence of petroleum hydrocarbons. Typical background values for this ratio are >5, as reported by Boehm (1981).

4. Saturate Hydrocarbon Weathering Ratio (SHWR)

$$\text{SHWR} = \frac{\text{sum of n-alkanes from nC12 to nC25}}{\text{sum of n-alkanes from nC17 to nC25}}$$

The SHWR approaches 1.0 as low-boiling saturated hydrocarbons (nC12-nC17) are lost by evaporation.

5. Carbon Preference Index (CPI)

$$\text{CPI} = \frac{2\,(nC27 + nC29)}{nC26 + 2\,nC28 + nC30}$$

CPI 1.0 for petroleum

CPI ranges from 3-6 for terriginous waxes, reflecting the formation mechanism for long chain hydrocarbons.

6. Aromatic Weathering Ratio

$$\text{AWR} = \frac{\text{Alkyl benzenes + naphthalenes + fluorenes phenanthrenes + dibenzothiophenes}}{\text{Total phenanthrenes + dibenzothiophenes}}$$

The AWR approaches 1.0 as low boiling aromatics are lost by evaporation and/or dissolution.

7. Σ PAH = summation of 4 and 5-ring PAH.

8. Total PAH = summation of alkyl naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes and PAH.

Table 9.5
Diagnostic Ratios for Lagomedio Crude

	Fresh Oil	Aged Oil
Saturates		
SHWR	2.87	2.28
ALK/ISO	2.36	2.50
PRIS/PHYT	0.85	0.74
C18/PHYT	1.64	1.61
Aromatics		
AWR	4.29	3.47

Table 9.6
GC/MS Analytical Conditions

Column:	25 m x 0.25 mm BP-5 5% phenyl, polydimethyl siloxane bonded phase fused silica column (S.G.E.).
Carrier Gas:	helium
Injector Flow Rate:	60 mL min-1
Injector Pressure:	17 p.s.i.g.
Column Flow:	40 cm s-1
Split Ratio:	40:1 (approximately)
Injector Temperature:	260° C
Injection Sequence:	splitless injection at room temperature, splitting resumed at 1 minute, 100° C at 2 minutes and 10° min-1 at 4 minutes to 280° C and hold for 10 minutes. 0.5 µL injections.
Mass Spectrometer:	electron impact source
Source Emission	0.50 mA
Electron Energy:	40 eV
Operating Pressure:	1 x 10^{-5} torr
Multiplier Voltage:	2000 V (gain > 10^6)
Data System:	data are acquired in the continuous scan mode from 40 to 350 amu from 4 min after sample injection, or, for SIM, one scan per second for four selected ions, with five pre-selected clusters of four ions each
Acquisition Rate:	one scan of 4 selected ions per second, 5 clusters of 4 ions

The GC conditions used provides adequate separation (i.e., resolution with 10% valley or better) for the following isomers:

phenanthrene/anthracene

benz(a)anthracene/chrysene

benzo(e)pyrene/benzo(a)pyrene/perylene

Table 9.7
Limit of Detection for Selected PAH

Compound	Detection Limit (ng/sample)
naphthalene	0.25
fluorene	0.5
phenanthrene	0.5
pyrene	0.5
chrysene	1.0
benzo(a)pyrene	1.0
perylene	1.0

Figure 9.2
GC/MS SIM Plots

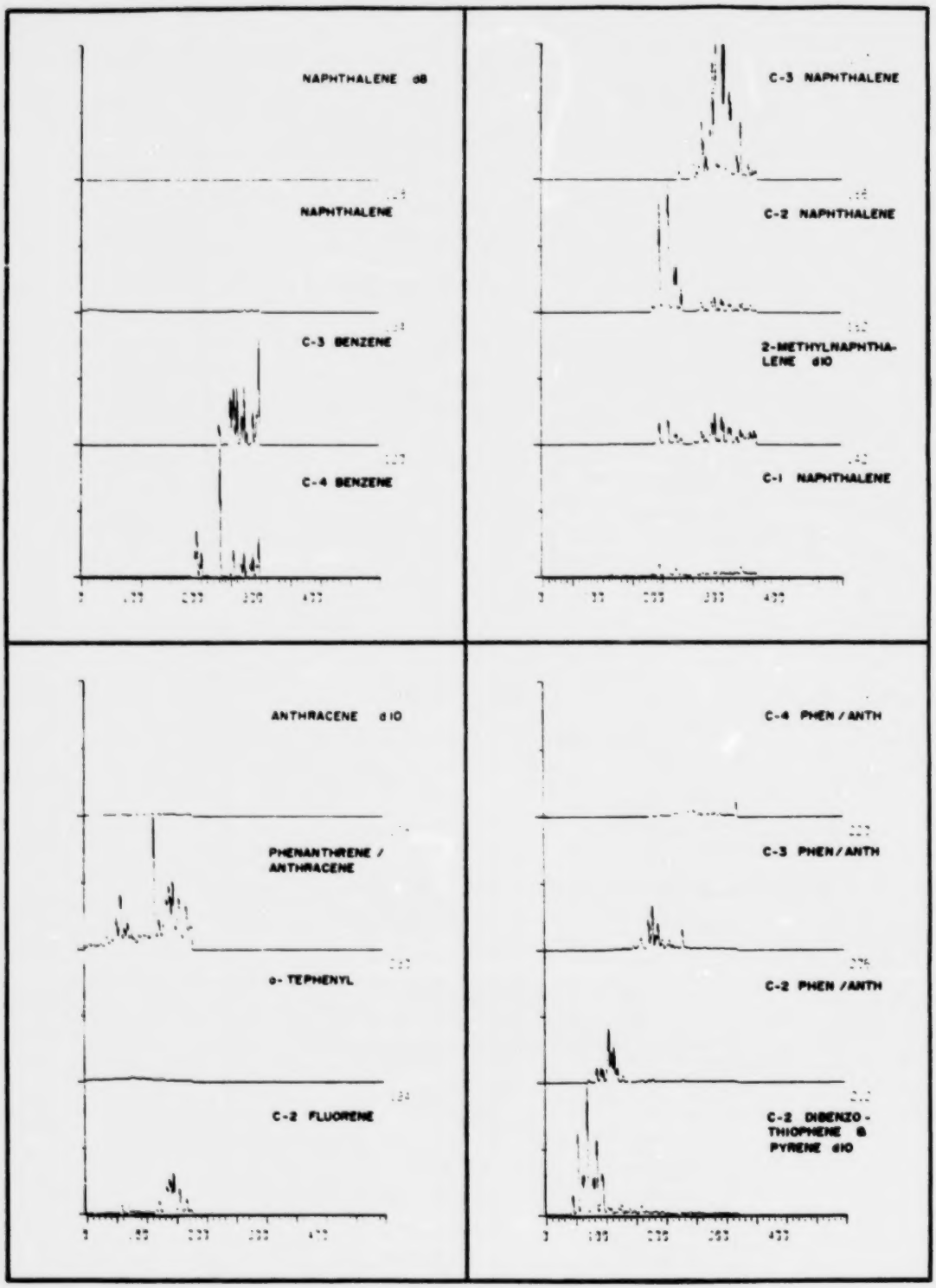
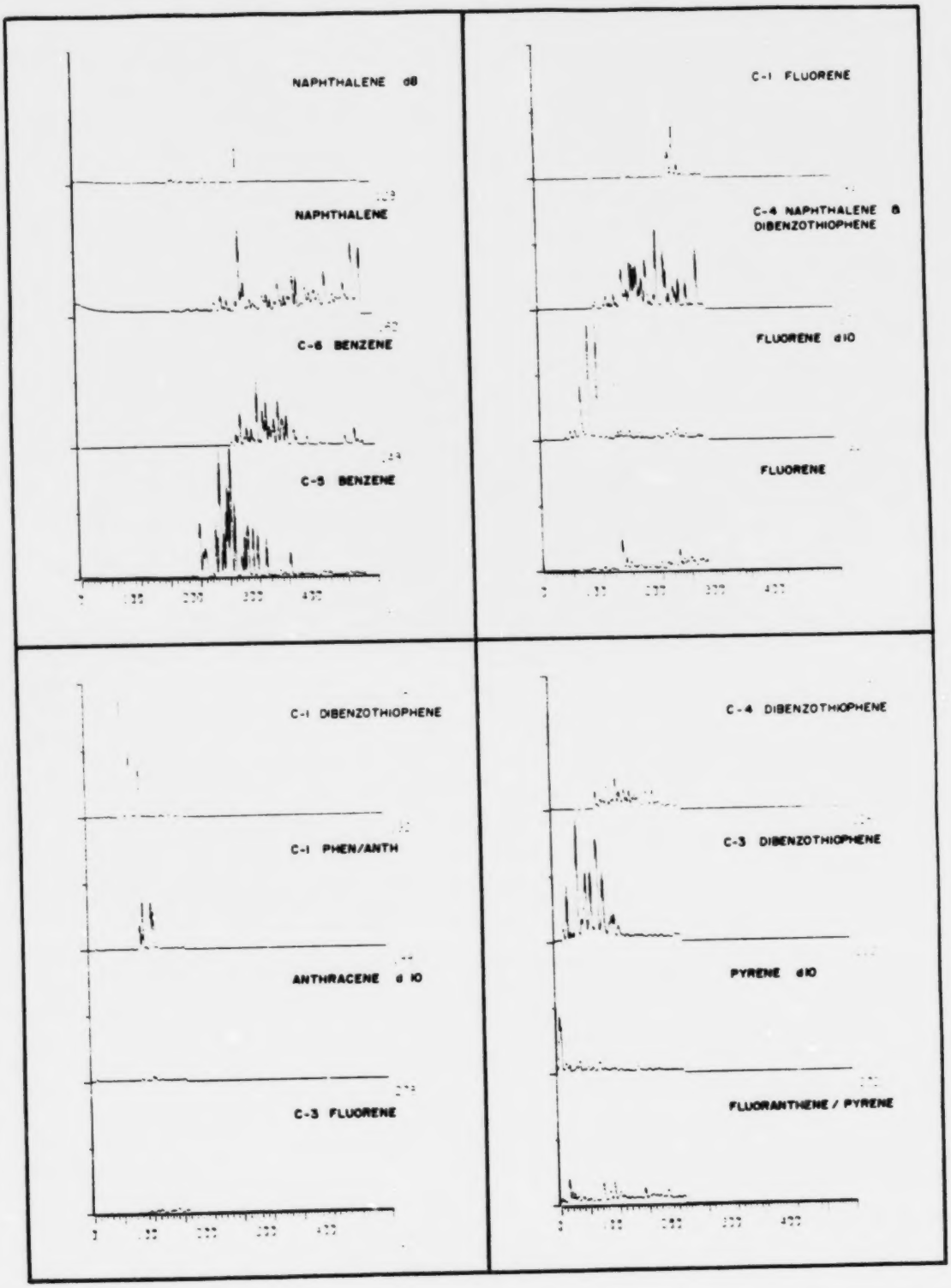


Figure 9.2
GC/MS SIM Plots



GC/MS analysis. GC/MS analysis was used to determine concentrations of various alkylated (C1-C4) and parent polycyclic aromatic hydrocarbons (PAH), as well as alkylated (C3-C6) benzenes. Alkylation patterns derived from the data were used to infer the presence of oil. If oil was present, the aromatic weathering ratio (Table 9.4) was used to determine the extent of its weathering. Typical values of this ratio for fresh and aged oil are given in Table 9.5.

The polar fraction (f-2) from selected samples was analysed by capillary column gas chromatography on a Finnegan 9500/3000 GC/MS equipped with a splitless injection port. The column exits at the ion source. Instrumental conditions are listed in Table 9.6 and limits of detection for selected PAH are given in Table 9.7.

Data was acquired in the Selective Ion Monitoring (SIM) mode for parent ions of those compounds of interest. Identification was based on known retention indices as well as being in the correct ion window. The SIM plots obtained from a typical sediment extract are shown in Figure 9.2. Quantification was based on comparing integrated peak areas with the area of an internal standard (perdeuterated PAH). Relative response factors were calculated from daily calibration runs. Concentrations were converted to a dry weight basis.

10. RESULTS

10.1 Bay 11

Data from Bay 11 Subtidal Profile sediments is presented in Table 10.1. Data from Bay 11 Deep Sediments is presented in Table 10.2.

10.2 Bay 9

Data from Bay 9 Diffuser Area sediment is presented in Table 10.2.

Table 10.1

WEATHERING INDICES
BAY 11 SUBTIDAL PROFILE SEDIMENTS

ID	PROFILE	DEPTH m	DISTANCE m *	SHWR	ALK ISO	C18 PHYT	PRIS PHYT	CPI	AWR	[OIL] (UV/F) mg/kg	OIL? (Subjective)
5164	1 (Bunch)	Low tide	ridge	1.0	0.3	0.3	0.3	1.0	N/A	66	+
5162	1 (Bunch)	1	15	1.7	2.2	1.4	0.7	1.3	1.6	7600	+
5165	1 (Bunch)	2	20	1.1	0.6	0.5	0.8	1.4	1.1	640	+
5170	1 (Bunch)	5	25	1.1	1.8	2.7	4.8	5.5	N/A	14	-
5161	1 (Bunch)	3	30	1.4	0.6	0.4	0.6	1.4	1.3	2800	+
5163	1 (Bunch)	5	35	1.1	1.7	1.4	2.8	4.0	N/A	27	-
5071	1 (Bunch)	4	50	1.1	0.4	0.3	0.5	1.4	N/A	280	+
5167	1 (Bunch)	6	80	1.0	1.2	0.9	1.5	3.4	1.3	36	?/-
5168	1 (Bunch)	7	100	1.1	0.3	1.6	23.0	3.3	N/A	14	?/-
5169	1 (Bunch)	9	120	1.0	1.4	1.9	3.6	3.8	N/A	2	?/-
5166	1 (Bunch)	12	140	1.1	1.6	2.4	11.0	4.5	N/A	15	-
5172	2 (South)	12	84	1.0	1.0	1.2	1.3	4.0	1.4	38	-
5171	2 (South)	9	67	1.0	1.3	1.3	2.4	3.7	N/A	18	?/-
5175	2 (South)	5	27	1.1	1.3	0.9	2.6	4.5	N/A	24	-
5173	2 (South)	3	19	1.0	1.0	1.5	10.0	4.8	N/A	9	-
5174	2 (South)	1	4	1.0	0.2	0.6	9.0	4.8	N/A	15	-
5178	3 (Centre)	12	168	1.0	1.8	1.6	2.5	2.3	2.1	15	+
5176	3 (Centre)	9	141	1.0	2.1	3.3	4.2	3.5	1.1	13	?/+
5177	3 (Centre)	5	70	1.0	0.8	1.4	4.3	4.8	N/A	7	-
5179	3 (Centre)	3	38	1.1	0.6	0.9	3.7	2.6	N/A	18	+
5180	3 (Centre)	1	4	1.1	0.6	0.6	0.8	1.4	1.1	93	+

*: Estimated distance from low tide line

Table 10.2

WEATHERING INDICES
OTHER SUBTIDAL SEDIMENTS

ID	SAMPLE	SHWR	ALK ISO	C18 PHYT	PRIS PHYT	CPI	AWR	[OIL] (UV/F) mg/kg	OIL? (Subjective)
BAY 11 DEEP SEDIMENTS									
5155	Bay 11 Deep Sediment 1	1.0	1.3	1.5	1.3	0.6	1.3	27	+
5156	Bay 11 Deep Sediment 2	1.1	1.8	1.9	3.1	5.8	N/A	11	-
5157	Bay 11 Deep Sediment 3	1.0	1.8	1.8	1.2	7.6	N/A	9	-
5158	Bay 11 Deep Sediment 4	1.1	1.7	2.9	11.0	5.3	N/A	16	-
5159	Bay 11 Deep Sediment 5	1.0	1.1	1.9	5.3	5.7	1.7	40	-
5160	Bay 11 Deep Sediment 6	1.1	1.4	1.5	3.7	4.4	N/A	22	-
BAY 9 DIFFUSER AREA SEDIMENTS									
5229	20m N, 5m depth	1.1	0.9	5.2	26.0	3.8	N/A	7	-
5230	20m N, 10m depth	1.1	0.9	2.8	11.0	4.5	N/A	8	-
5231	5m depth	1.0	1.0	3.0	13.0	5.4	N/A	7	-
5232	10m depth	1.1	1.4	4.6	12.0	3.2	N/A	6	-

11. DISCUSSION

The expectation that the observed petroleum hydrocarbons found in the subtidal sediments of Bay 11 were increasing in 1982 due to transport from the intertidal sediments was tested in 1983 by analysing samples collected along the southern Microbiology transect (the Bunch transect). The results indicated that there were some areas with high concentrations of petroleum hydrocarbons, and other areas where the concentrations were lower, but distinguishable as petroleum in origin. The indicators used were the presence of an unresolvable complex mixture (UCM), the presence of phytane, a low Carbon Preference Index (CPI), and included some subjectivity on the part of the chemist.

In 1983, the concentrations ranged from 0.8 to 410 ug/g calculated from the phytane concentration, based on the observed concentration of phytane in aged Lagomedio crude oil (phytane = 6.4 mg/g oil). Background concentrations of phytane were about 0.001 ug/g sediment. The oil was present in substantial quantities down to about 7 m depth. Higher concentrations were more biodegraded than lower concentrations, based on C_{18}/phytane ratios. In some samples, oil was indicated by the presence of phytane where other material masked it.

In 1985, we again observed definite indications of oil present in subtidal sediments from the Bunch transect to 7 m depth. Figure 11.1 indicates the total hydrocarbon values for the samples colleced from all three transects. Those marked with an * are those for which oil is subjectively determined as present. Indicators are the presence of a UCM, low CPI, and the presence of phytane, although the background concentrations as measured appear to be slightly higher (0.009 ± 0.01 ug/g sediment). Comparison of 1983 results show similar distribution on that transect, although the exact comparison of positions was not possible due to movement of the sample line on the bottom.

A direct comparison of concentrtions based on the phytane equivalent is possible, and is presented in Table 11.1. The distances from shore for 1983 are estimated from Figure 3.12 in Boehm *et al.* (1984). The values for both years are based on calculations from the reported phytane concentrations and the factor of 151 ug oil per ug phytane.

Using phytane as the prime indicator for the presence of oil is becoming less tenable with time. The background concentration of phytane in environmental samples is variable, and the phytane from the released oil may be degrading by this time, especially in samples where the n-alkanes are depleted.

Figure 11.1

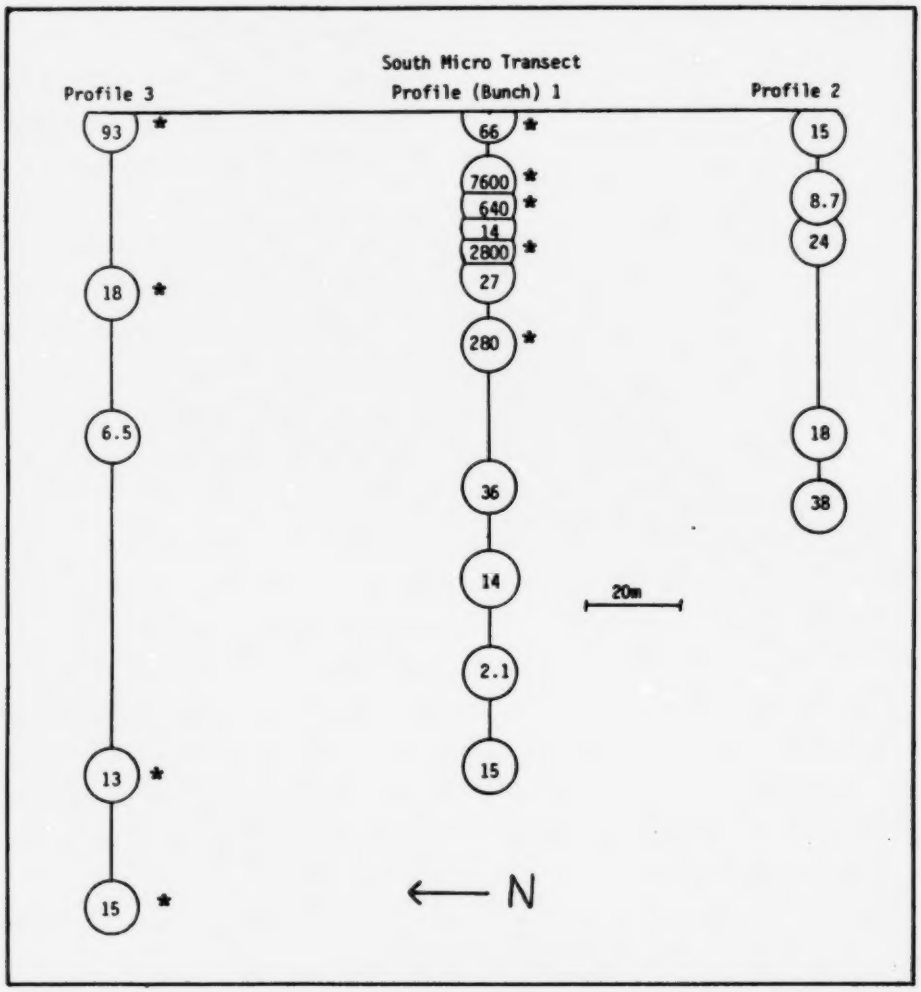

South Micro Transect
Profile 3
Profile (Bunch) 1
Profile 2
93
18
6.5
13
15
66
7600
640
14
2800
27
280
36
14
2.1
15
15
8.7
24
18
38
20m
N

Table 11.1.

Comparison Between 1983 and 1985

Depth (m)	Distance from Shore (m)	1983 Total HC ug/g	1983 Est. Oil ug/g	1985 Total HC ug/g	1985 Est. Oil ug/g
1	2	63	255		
2	4	24	44	66	14
2	9	300	405		
1	15			7,600	2,400
2	20			640	102
4	25	65	117	14	1
3	30			2,800	720
5	35			27	1
5	39	30	36		
5	42	30	42		
5	44	35	41		
4	50			280	315
6	65	34	29		
6	78	13	5		
6	80			36	5
6	85	8	4		
7	95	5	1		
7	100			14	1
8	105	5	2		
9	120			2	1
9	125	7	1		
9	127	8	1		
11	140	7	1	15	1
11	147	4	2		

The new transect sampled in 1985 in the center of the experimental area also indicated the presence of significant concentrations of oil. While higher concentrations were found near the shore, the sample from 12 m depth also indicated that the measured hydrocarbons included petroleum hydrocarbons, as shown in the presence of a UCM and phytane.

The transect south of the experimental area did not indicate any significant presence of oil, nor did the 'Deep Sediments', with the possible exception of the sample from the station 1.

A comparison of the chromatograms obtained in 1985 with the examples shown for the 1983 samples indicates a general similarity. Some of the samples are more weathered than others, although the higher concentration samples in 1985 did not show the greater degree of weathering comapred to lower concentrations that was observed in 1983.

The concentrations of hydrocarbon in the subtidal sediments do not appear to be changing markedly. It is possible that a quasi-steady state has been established, with new input balanced by transport out of the area.

12. REFERENCES

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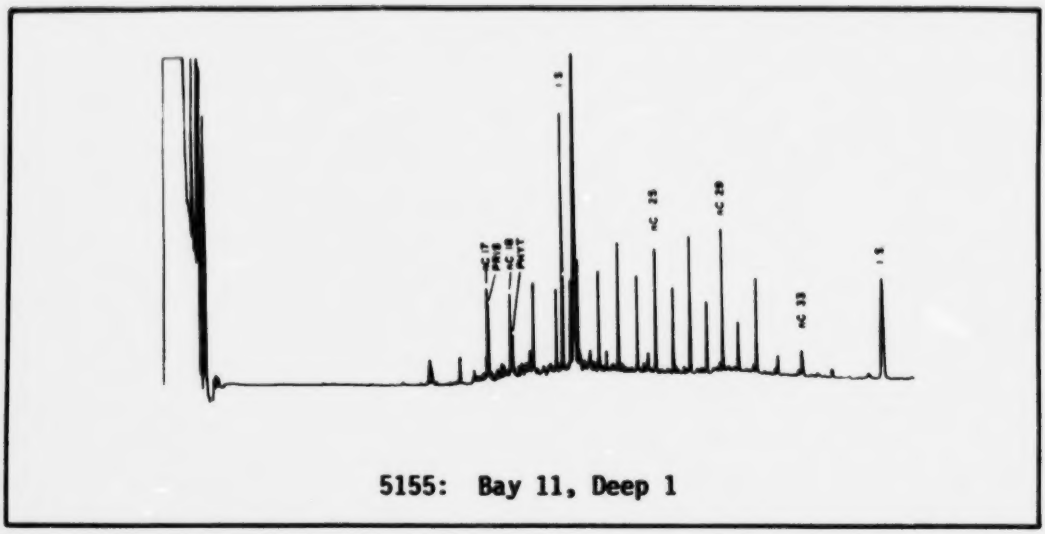
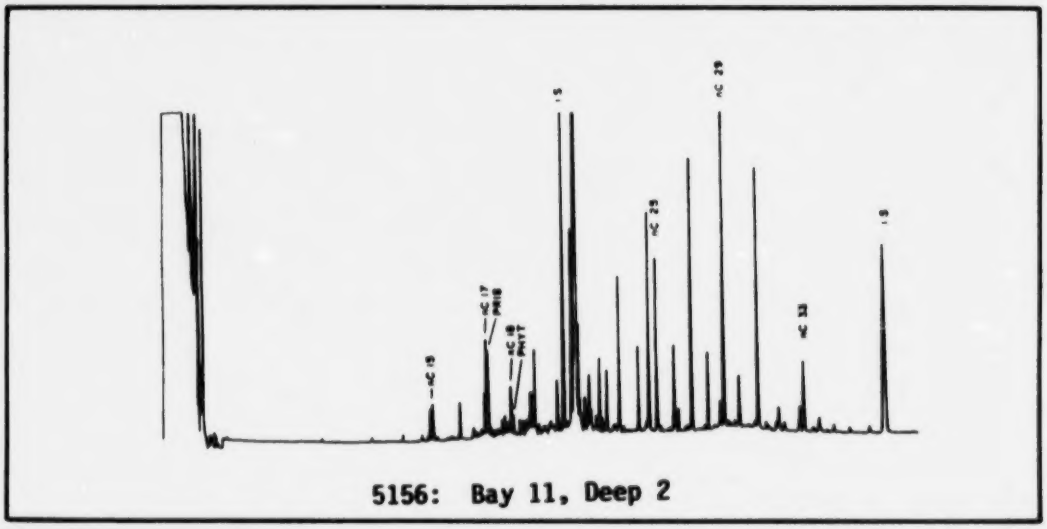
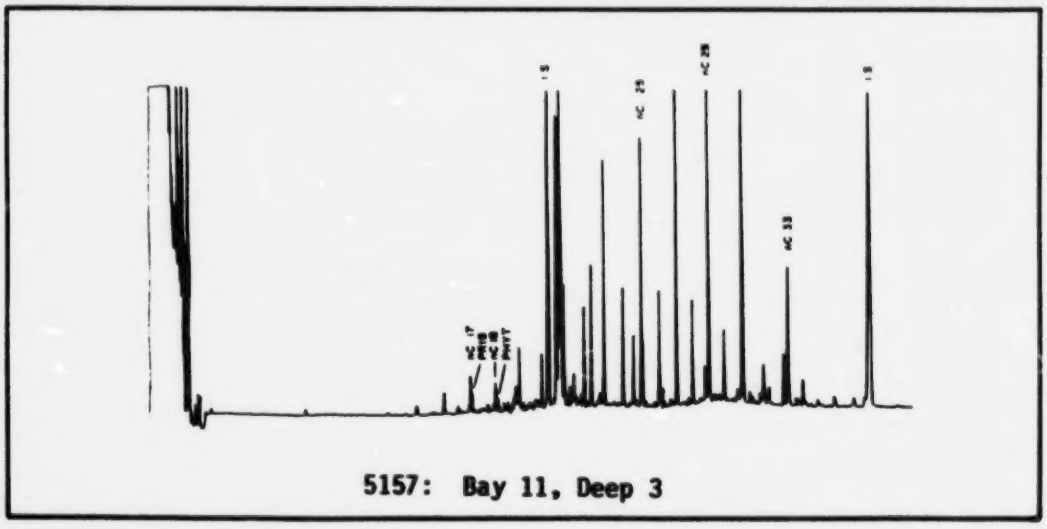
APPENDIX C: GAS CHROMATOGRAPHY



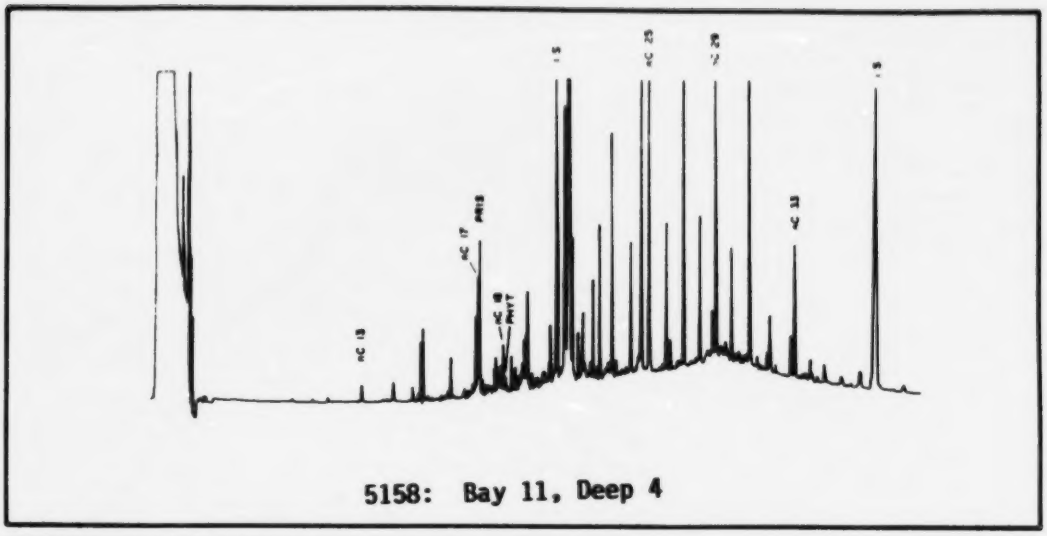
5155: Bay 11, Deep 1



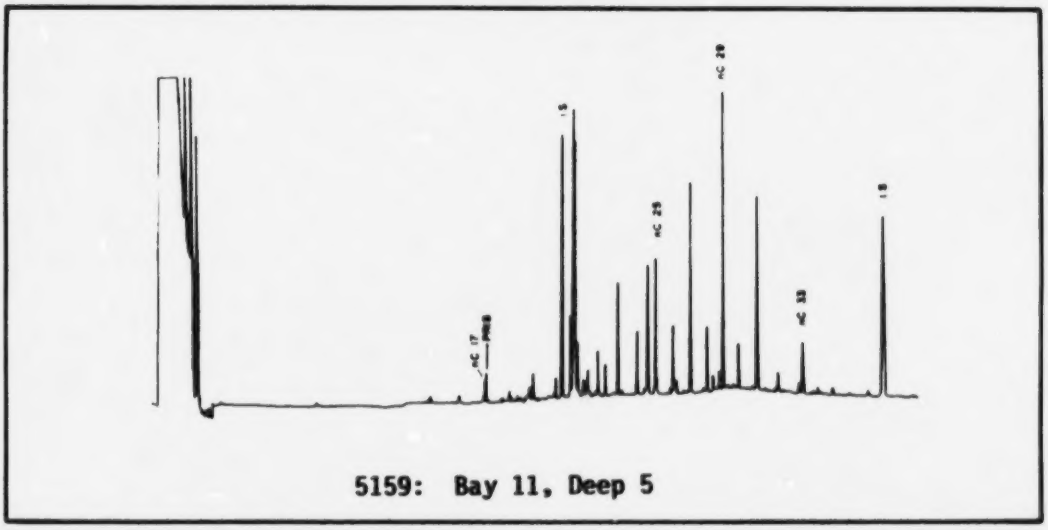
5156: Bay 11, Deep 2



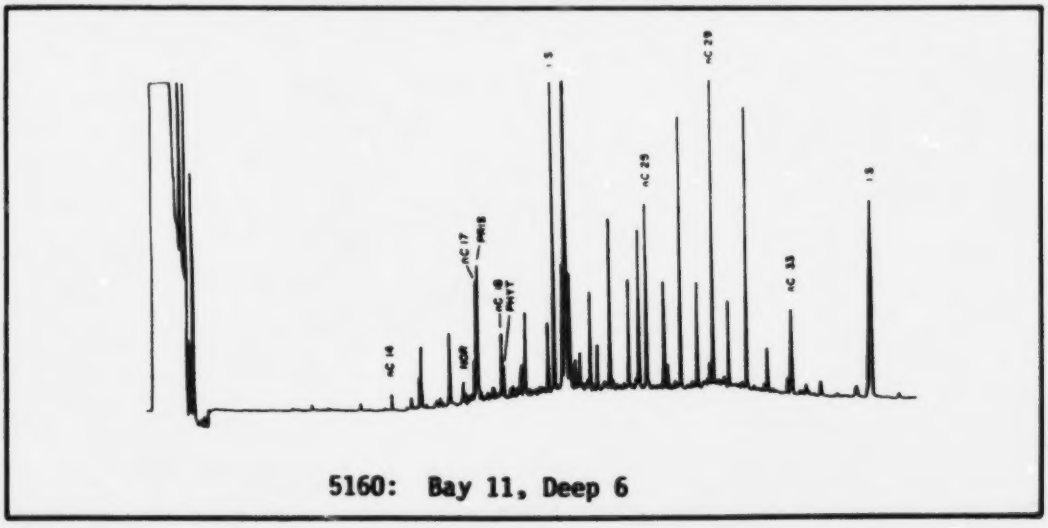
5157: Bay 11, Deep 3



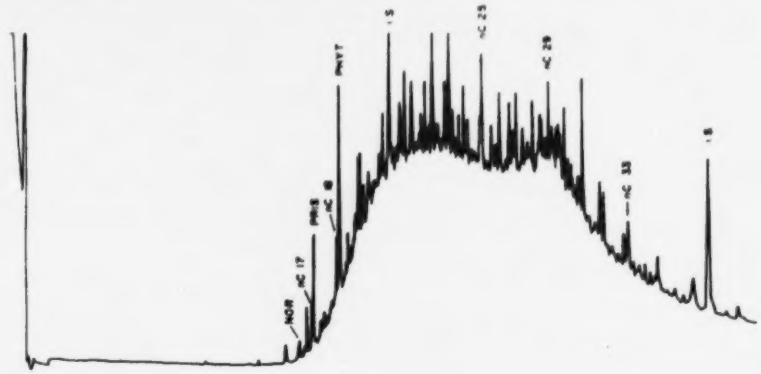
5158: Bay 11, Deep 4



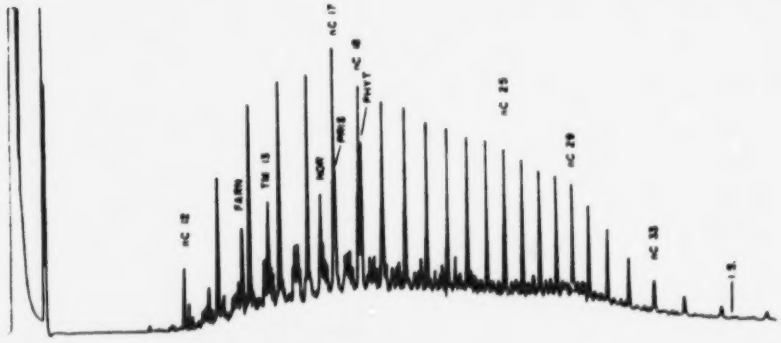
5159: Bay 11, Deep 5



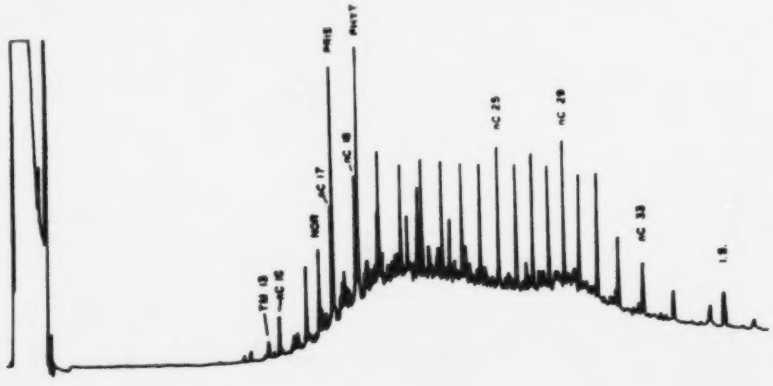
5160: Bay 11, Deep 6



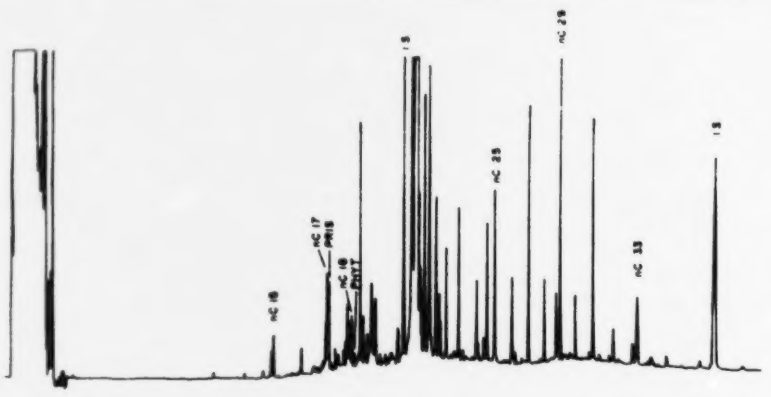
5164: Bay 11, Profile 1 (Bunch) 4, Low Tide Ridge



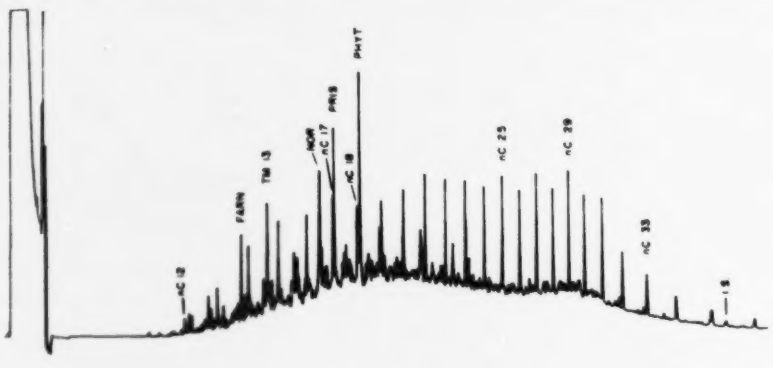
5162: Bay 11, Profile 1 (Bunch) 2, 1M Depth, 15M



5165: Bay 11, Profile 1 (Bunch) 5, 1.5M Depth, 20M



5170: Bay 11, Profile 1 (Bunch) 10, 5M Depth, 25M



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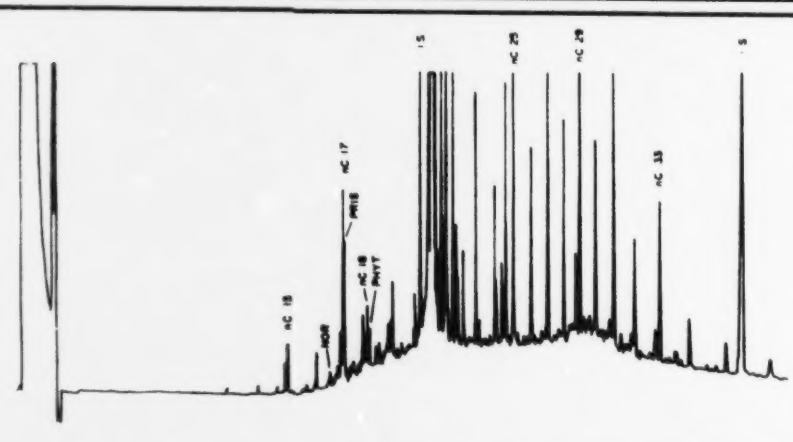
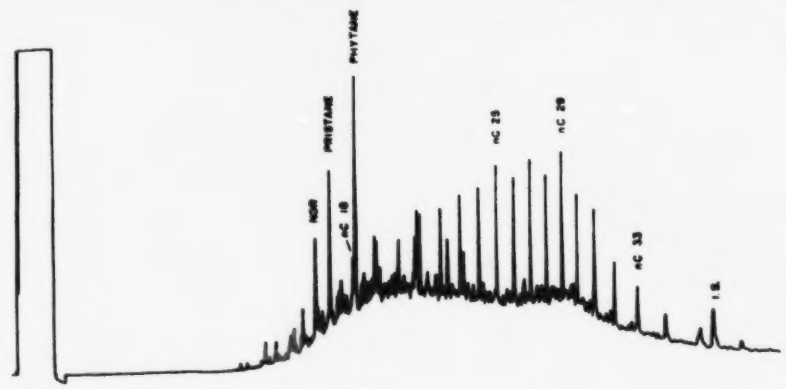
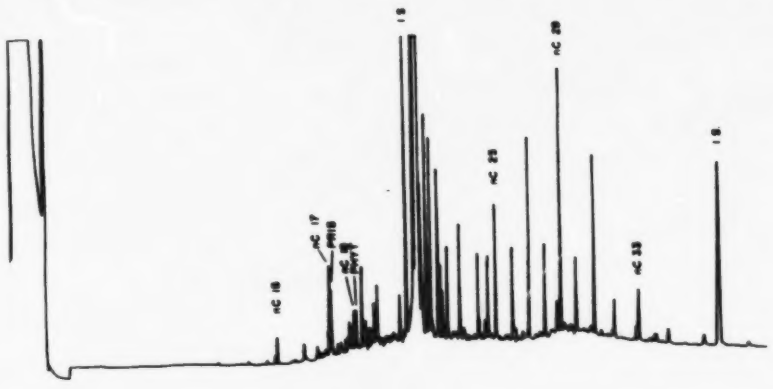


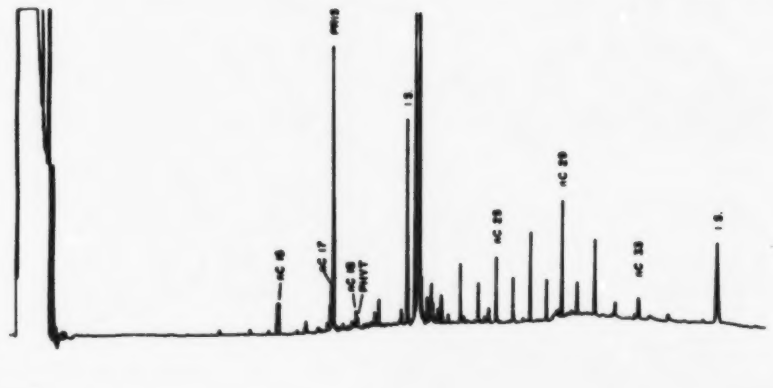
5163: Bay 11, Profile 1 (Bunch) 3, 5M Depth, 35M



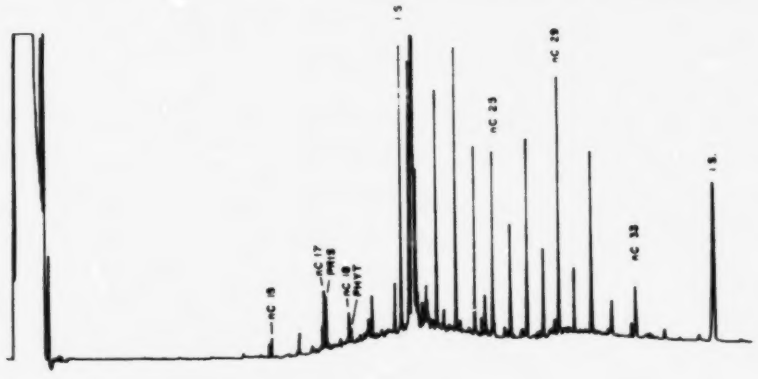
5071: Bay 11, Profile 1 (Bunch), 4M Depth, 50M



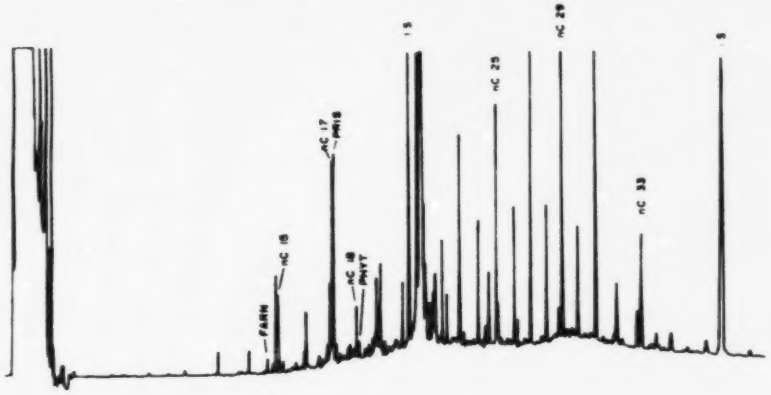
5167: Bay 11, Profile 1 (Bunch) 7, 5.5M Depth, 80M



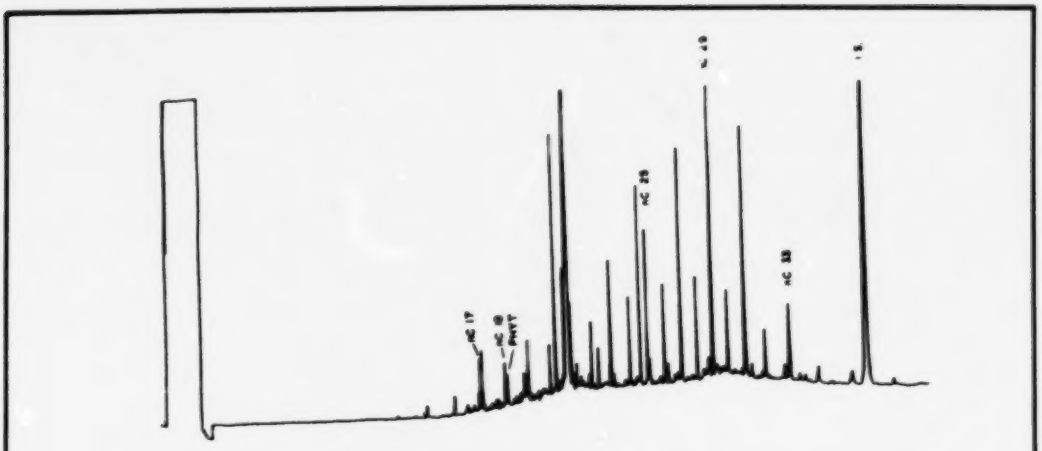
5168: Bay 11, Profile 1 (Bunch) 8, 6.5 M Depth, 100M



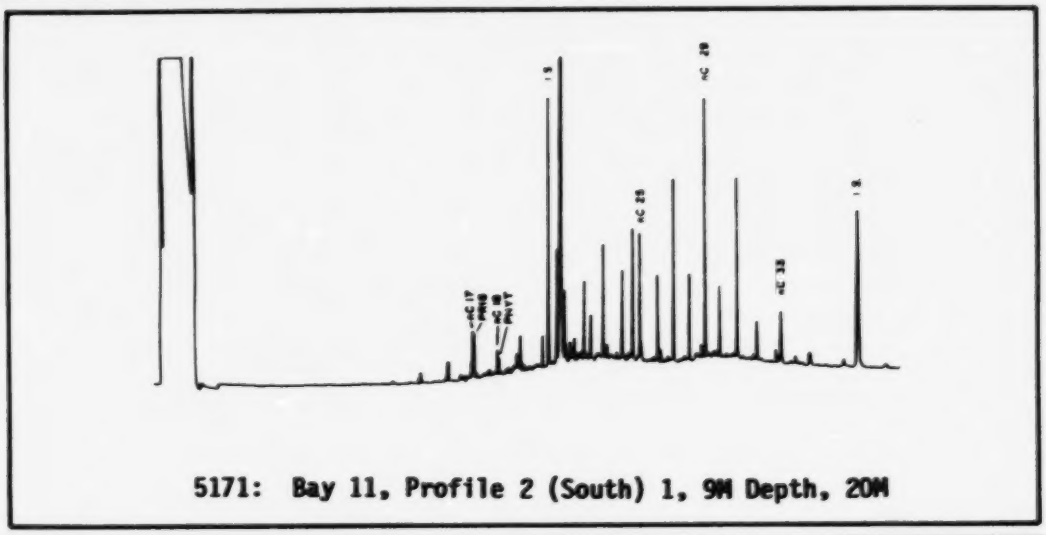
5169: Bay 11, Profile 1 (Bunch) 9, 9M Depth, 120M



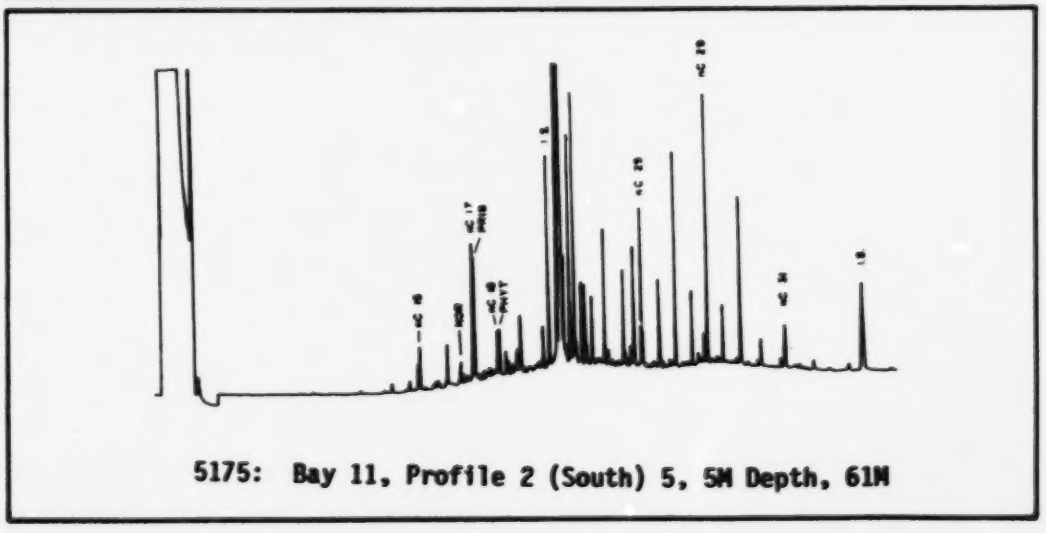
5166: Bay 11, Profile 1 (Bunch) 6, 12M Depth, 140M



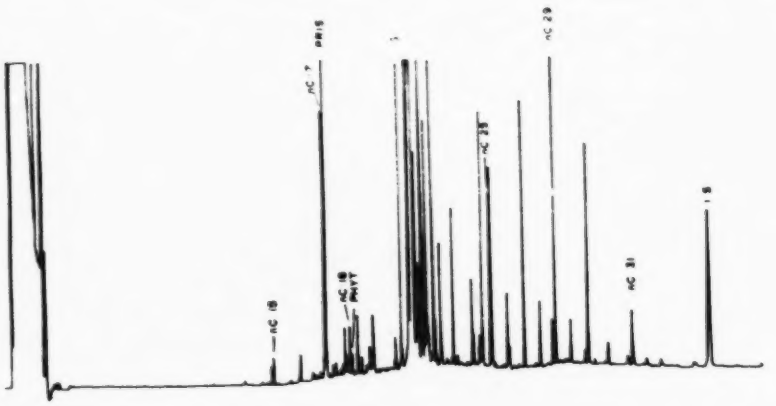
5172: Bay 11, Profile 2 (South) 2, 12M Depth, 5M



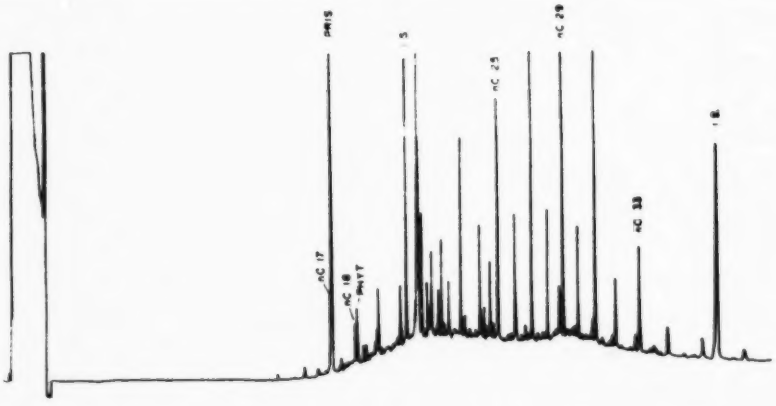
5171: Bay 11, Profile 2 (South) 1, 9M Depth, 20M



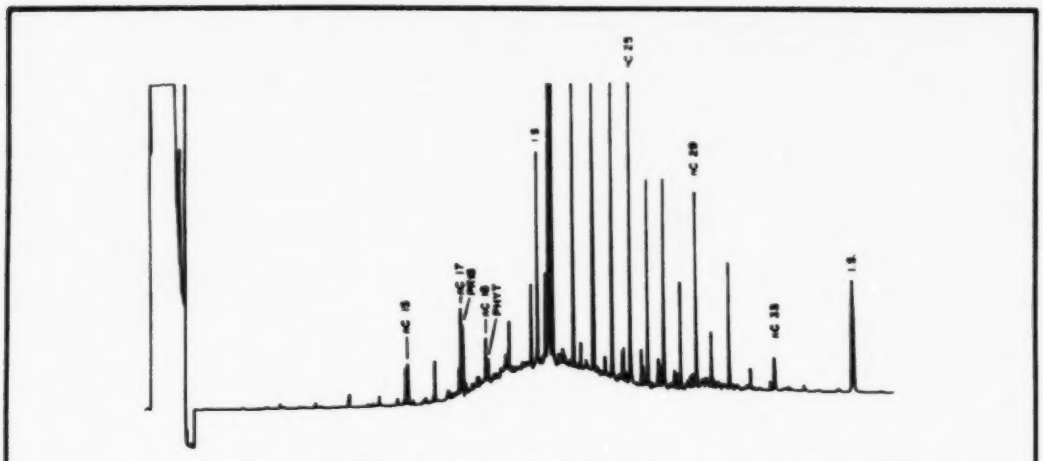
5175: Bay 11, Profile 2 (South) 5, 5M Depth, 61M



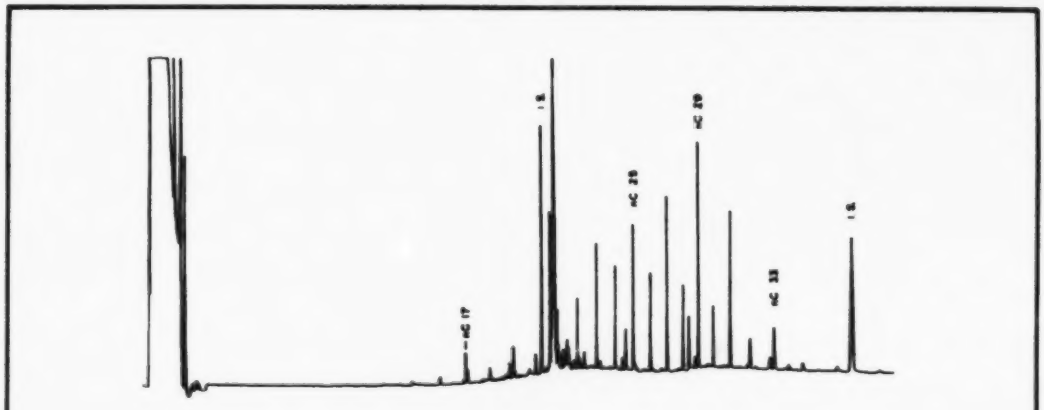
5173: Bay 11, Profile 2 (South) 3, 3M Depth, 70M



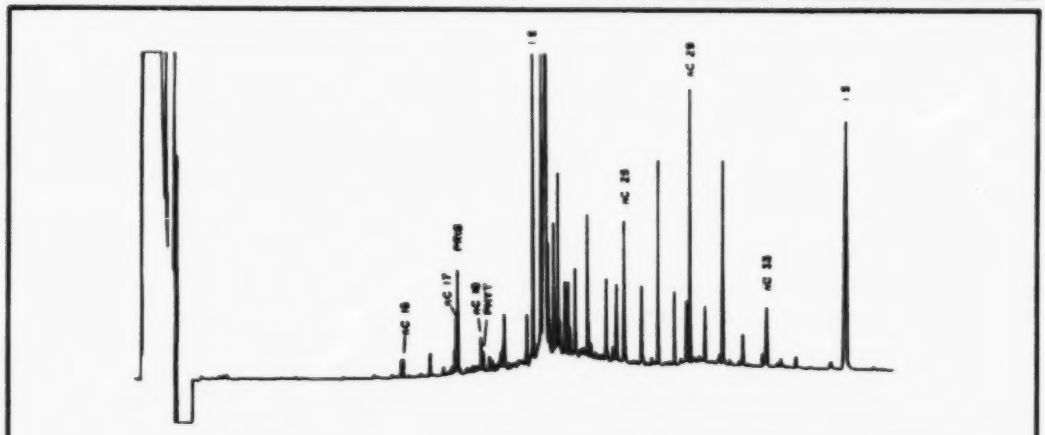
5174: Bay 11, Profile 2 (South) 4, 1M Depth, 89M



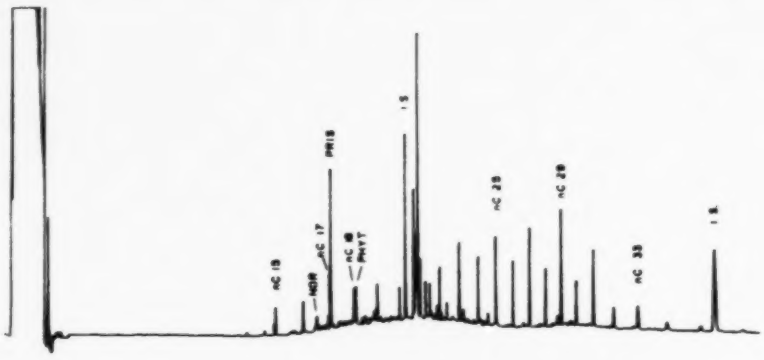
5178: Bay 11, Profile 3 (Centre) 3, 12M Depth, 0M



5176: Bay 11, Profile 3 (Centre) 1, 9M Depth, 28M



5177: Bay 11, Profile 3 (Centre) 2, 5M Depth, 100M



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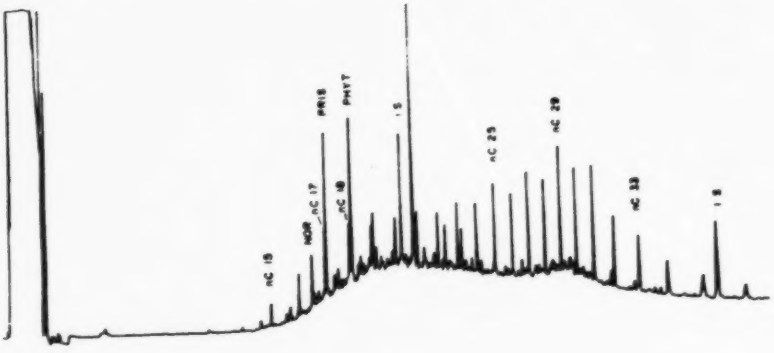
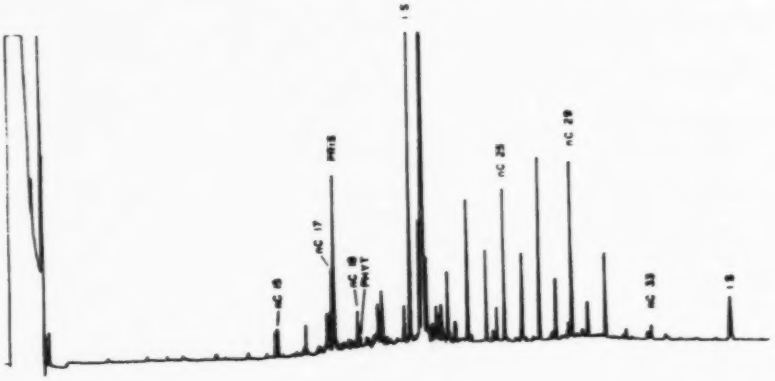
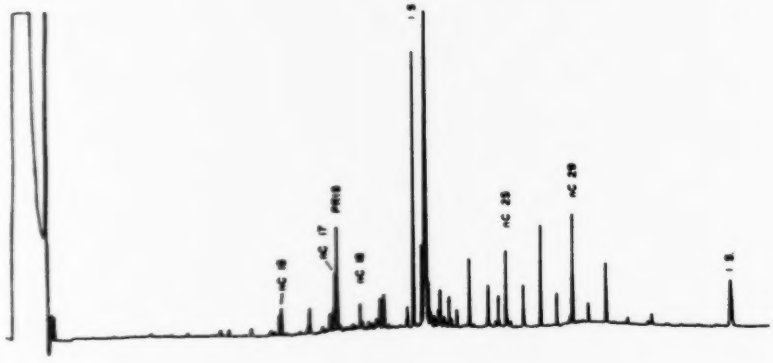


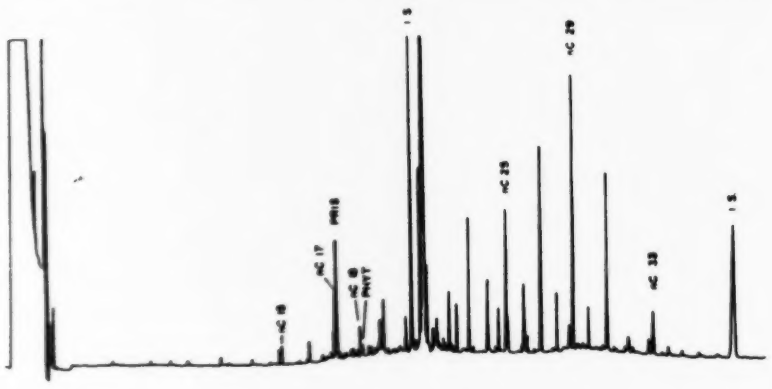
5180: Bay 11, Profile 3 (Centre) 5, 1M Depth, 169M



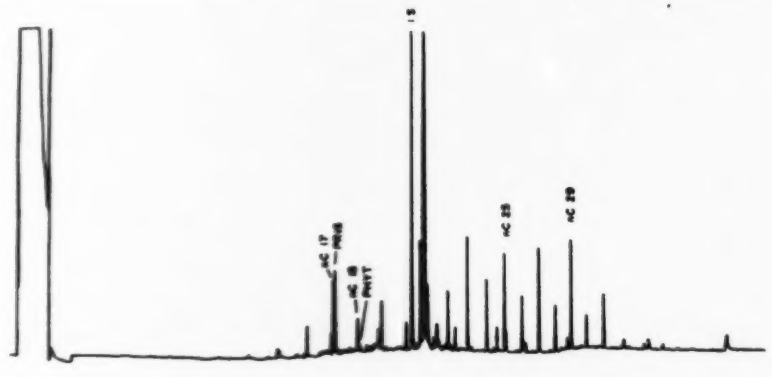
5229: Bay 9, Diffuser, 5M Depth



5230: Bay 9,20M North of Diffuser, 5M Depth



5231: Bay 9,20M North of Diffuser, 10M Depth



5232: Bay 9, Diffuser, 10M Depth

APPENDIX D: DATA SUMMARIES

ALKANE SUMMARY

Sub-Tidal Sediment Profiles
(ng g-1 dry weight)

Compound	5155	5156	5157	5158	5159	5160	5161	5162	5163	5164	5165	5166	5167	5168	5169	5170
nC12	< 3	< 1	< 1	< 1	< 2	< 2	210	4600	< 0.9	< 1	< 8	0.9	< 3	< 3.8	< 2	< 1
nC13	< 3	< 1	< 1	2.1	< 2	2.1	840	17000	0.9	< 1	< 8	3.4	< 3	3.8	< 2	< 1
nC14	< 3	1.6	< 1	2.4	< 2	4.8	1700	30000	1.6	< 1	18	3.7	< 3	3.9	< 2	< 1
nC15	6	4.9	1.7	10	< 2	19	1700	29000	8.0	< 1	65	13	13	15	3.7	10
nC16	12	7.5	4.0	5.5	4.2	21	1600	26000	6.7	4.5	150	11	9.3	6.0	6.7	6.7
nC17	48	24	5.4	19	8.1	48	1900	27000	39	11	270	39	60	21	17	23
nC18	54	14	5.8	6.4	4.8	23	1700	23000	13	26	340	8.9	26	16	10	13
nC19	65	25	13	16	14	32	1300	22000	15	27	260	18	41	21	17	17
nC20	62	16	12	9.3	12	30	2000	18000	11	20	290	13	33	14	19	10
nC21	82	35	26	26	31	50	1900	16000	51	33	290	28	120	39	62	36
nC22	77	23	23	17	26	41	2000	13000	23	28	270	21	56	24	100	19
nC23	110	56	67	53	80	83	2000	14000	61	29	290	49	110	53	130	53
nC24	80	34	34	27	49	60	2000	12000	34	25	290	29	74	39	90	29
nC25	120	66	88	73	99	110	2600	13000	81	52	390	65	140	64	92	60
nC26	91	41	42	41	58	67	2700	14000	56	53	400	41	100	57	58	36
nC27	140	130	160	130	180	170	2700	12000	140	30	380	110	200	100	100	100
nC28	71	38	40	44	57	64	2400	1100	62	27	350	40	92	48	35	35
nC29	150	200	280	210	280	270	3000	12000	230	35	430	170	290	140	150	160
nC30	67	35	35	41	50	64	3000	11000	68	48	410	41	98	44	38	27
nC31	130	200	290	210	260	260	3200	9700	210	78	520	170	270	130	140	150
nC32	41	25	33	30	32	45	2100	6600	55	69	350	37	68	33	28	23
nC33	65	77	110	85	100	110	2300	6100	94	50	360	74	110	47	62	59
nC34	18	5.5	3.6	11	12	20	1200	3700	26	58	200	12	33	15	11	8
nC35	< 6	< 3	< 2	< 2	< 6	< 5	< 150	4000	< 2	< 2	160	12	29	< 7	8.4	8
nC36	< 6	< 3	< 2	< 2	< 6	< 5	< 150	2300	< 2	< 2	110	5.2	< 7	< 7	< 4	< 3
FARN	< 3	< 1	< 1	< 1	< 2	< 2	1700	9800	< 0.9	< 1	7.7	< 0.9	< 3	< 4	< 2	< 1
TM13	< 3	< 1	< 1	< 1	< 2	< 2	670	14000	< 0.9	< 1	34	2.7	< 3	< 4	< 2	< 1
NORP	11	< 1	1.9	< 1	< 2	13	3100	11000	4.2	5.8	230	< 0.9	12	< 4	2.0	1.4
PRIS	46	22	9.0	20	14	57	3100	11000	26	31	560	41	44	220	19	21
PHYT	36	7.1	3.3	2.2	< 2	15	4800	16000	9.3	94	680	3.8	30	9.9	5.2	4.9

ALKANE SUMMARY

Sub-Tidal Sediment Profiles
(ng g-1 dry weight)

Compound	5171	5172	5173	5174	5175	5176	5177	5178	5179	5180	5229	5230	5231	5232	5071
nC12	< 2	< 3	< 3	< 1	< 4	< 2	< 0.7	< 1.5	< 4	< 2	< 5	< 5	< 1.6	<20	< 10
nC13	< 2	< 3	< 3	< 1	< 4	< 2	< 0.7	4.4	< 4	< 2	5.9	< 5	1.7	<20	< 10
nC14	< 2	< 3	< 3	< 1	6.2	< 2	< 0.7	3.2	< 4	< 2	6.6	6.2	1.7	<20	< 10
nC15	4	< 3	6.9	1.2	30	< 2	1.5	10	10	9	16	14	3.3	61	190
nC16	6	< 3	17	2.5	37	4.4	2.3	12	11	16	24	21	5.5	110	260
nC17	13	25	130	22	140	7.8	7.7	26	20	36	100	42	27	330	460
nC18	8	28	23	8.8	42	5.6	4.6	15	15	57	41	29	11	150	610
nC19	13	40	28	16	56	15	9.2	22	17	33	72	47	23	220	420
nC20	12	34	28	18	45	10	8.9	37	18	44	50	31	17	120	400
nC21	28	60	160	33	120	34	21	150	30	33	100	55	32	320	610
nC22	31	47	150	25	82	39	13	330	31	40	96	46	27	290	650
nC23	69	95	210	61	160	79	28	410	52	56	210	97	63	590	910
nC24	43	78	130	33	110	69	17	330	48	65	150	67	38	390	930
nC25	57	140	170	83	210	91	30	250	65	100	270	130	79	550	1300
nC26	44	91	97	50	120	69	19	150	61	100	170	78	45	360	1400
nC27	96	210	220	140	290	130	55	160	92	110	370	190	130	690	1400
nC28	46	90	69	43	100	60	20	93	56	110	130	63	40	300	1200
nC29	150	320	290	190	390	180	84	180	130	150	350	230	200	770	1400
nC30	43	82	43	43	82	48	19	60	52	160	81	45	39	240	1300
nC31	140	320	240	170	320	160	85	170	120	230	250	180	180	500	1600
nC32	31	66	31	30	58	34	13	32	37	140	30	19	23	100	1000
nC33	58	120	81	72	110	68	35	59	43	140	<12	<12	70	110	920
nC34	19	32	14	19	26	12	7.0	11	18	95	<17	<12	4.9	<40	680
nC35	13	27	< 7	18	16	8.0	6.0	< 6	12	74	<12	<12	< 4	<40	580
nC36	< 4	< 5	< 7	12	< 9	< 4	< 2	< 6	< 7	61	<12	<12	< 4	<40	260
FARN	< 2	< 3	< 3	< 1	< 4	< 2	< 0.7	< 1.5	< 4	< 2	< 5	< 5	< 1.6	<20	< 10
TM13	< 2	< 3	< 3	< 1	< 4	< 2	< 0.7	< 1.5	< 4	< 2	< 5	< 5	< 1.6	<20	56
NORP	2.0	< 3	5.3	1.5	32	< 2	1.8	4.7	8.7	30	6.6	6.7	< 1.6	41	690
PRIS	15	29	160	140	120	6.9	14	23	62	81	210	110	47	380	1000
PHYT	6.6	23	16	15	47	1.7	5.3	9.9	17	100	8.0	10	3.7	33	2100

PAH SUMMARY

Subtidal Sediments
(ng g^{-1} dry weight)

Compound	5155	5159	5161	5162	5165	5167	5172	5176	5178	5180
C-3 Benzene	2.2	3.1	< 5	< 7	<0.1	<0.03	0.61	1.4	<0.05	0.97
C-4 Benzene	0.34	<0.1	6.1	38	<0.1	<0.03	<0.5	<0.05	<0.05	0.12
C-5 Benzene	<0.06	<0.1	12	130	<0.1	<0.03	<0.5	<0.05	0.39	<0.02
C-6 Benzene	<0.06	<0.1	12	210	<0.1	<0.03	<0.5	<0.05	0.14	<0.02
C-0 Naphthalene	0.57	0.24	1.5	< 7	0.40	0.68	0.68	0.22	0.62	0.21
C-1 Naphthalene	1.4	0.78	26	52	2.1	1.2	0.42	0.66	1.3	0.40
C-2 Naphthalene	2.6	1.3	150	4000	3.8	4.9	4.0	4.4	5.4	1.7
C-3 Naphthalene	0.56	<0.5	85	2000	3.5	0.061	3.8	2.2	2.9	2.7
C-4 Naphthalene	0.90	0.54	120	6200	6.9	1.5	3.1	0.26	0.91	1.5
C-0 Fluorene	0.50	0.29	4.9	< 20	0.32	0.41	0.67	0.30	0.49	0.12
C-1 Fluorene	0.85	0.42	17	500	1.8	0.84	1.3	0.45	0.44	0.30
C-2 Fluorene	1.4	1.3	135	5800	16	2.9	1.2	0.51	2.5	0.96
C-3 Fluorene	0.82	<0.02	26	260	3.7	0.35	2.4	0.12	0.48	0.97
C-0 Dibenzothiophene	0.60	0.44	17	170	1.6	0.95	1.1	42	0.48	0.38
C-1 Dibenzothiophene	1.8	0.68	0.69	1400	6.8	0.73	3.8	0.33	0.55	1.2
C-2 Dibenzothiophene	2.0	0.27	130	3600	15	1.8	3.2	0.77	1.2	11
C-3 Dibenzothiophene	3.0	0.78	180	1900	39	2.6	9.3	0.91	1.1	11
C-4 Dibenzothiophene	1.1	0.34	96	890	20	0.72	4.3	0.37	0.45	5.3
C-0 Phen/Anthracene	1.8	1.1	18	390	1.4	1.5	2.4	27	2.4	0.54
C-1 Phen/Anthracene	7.0	4.3	160	3600	15	3.5	3.8	3.8	5.6	4.4
C-2 Phen/Anthracene	7.7	1.3	240	6600	26	11	10	6.0	5.9	13
C-3 Phen/Anthracene	11	2.6	520	12000	80	16	6.4	2.5	1.5	14
C-4 Phen/Anthracene	9.7	<0.3	330	4500	120	<0.9	3.7	0.97	1.6	7.9

LONG TERM FATE AND PERSISTENCE OF STRANDED OIL AT CAPE HATT, N.W.T. AND FROM THE AMOCO CADIZ SPILL

Part 3: Amoco Cadiz

D. Hope
B. Humphrey
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TABLE OF CONTENTS

		Page
13.	INTRODUCTION	13/14/15-1
14.	METHODOLOGY	
	14.1 Sampling	13/14/15-1
	14.2 Analysis	13/14/15-1
15.	RESULTS	13/14/15-1
16.	DISCUSSION	16/17-1
17.	REFERENCES	16/17-1
	APPENDIX E: Gas Chromatography	E-1

13. INTRODUCTION

An opportunity to collect samples from the site of the Amoco Cadiz oil spill was taken by Owens and Robson (1985). The observation of the development of an asphalt pavement at the upper intertidal area at the Baffin Island Oil Spill Bay 11 site was reminescent of similar observations at the Amoco Cadiz site. Some samples were analysed by IR for total hydrocarbon, and some by gas chromatography and gas chromtography/mass spectrometry, to permit a comparison of the fate of standard oil in temperate versus arctic climates.

14. METHODOLOGY

14.1 Sampling

Sampling information is reported by Owens and Robson (1985).

14.2 Analysis

Analytical techniques used for these samples are described in Part 1, Appendices A and B.

15. RESULTS

Twenty samples were analysed for total hydrocarbons by Infra-red spectroscopy. The results are found in Table 15.1. Fourteen compositional GC/FID's were run. The chromatographs are found in the Appendix.

The majority of GC samples show a double humped unresolved complex mixture (UCM) with maximum in the range of nC20 and nC29. They do not have fine structure (i.e. n-alkanes, isoprenoids). The hopanes (pentacyclic triterpanes) are the only identifiable group of compounds. They are found in the nC27 to nC33 range.

There are four unusual samples amoungst these run by GC/FID. Sample No. 10 shows an unstructured single humped UCM which maximizes around nC16. Sample No. 12 shows an alkane fine structure as well as a very large hopane cluster. Sample No. 22 contains a large UCM with isoprenoid fine structure. Sample No. 34 contains a suite of high molecular weight alkanes that dominate the field. They range from nC27 to nC38.

Table 15.1

Amoco Cadiz Total Hydrocarbons by IR

NUMBER	LOCATION	DESCRIPTION	DEPTH	DATE COLLECTED	THC/IR [OIL] (mg/kg)
1	Aber Benoit	SHWM	Surface	85-03-23	
2	Aber Benoit	NHWM	Surface	85-03-23	3300
3	Croix	MHWM	Surface	85-03-23	
4	Croix	MHWM	0-2 cm	85-03-23	
5	Croix	MHWM	2-8 cm	85-03-23	2300
6	Croix	NHWM	Surface	85-03-23	250
7	Croix	MHWM	Surface	85-03-23	
8	Ste. Marguerite		0-2 cm	85-03-23	
9	Ile Grande	N. side marsh	0-3 cm	85-03-24	6700
10	Ile Grande	Active channel	0-6 cm	85-03-24	
11	Ile Grande	S. side marsh, SHWM, -1.0M	0-2 cm	85-03-24	
12	Ile Grande	S. side marsh, SHWM, -0.5M	0-2 cm	85-03-24	120
13	Ile Grande	S. side marsh, SHWM	0-2 cm	85-03-24	
14	Ile Grande	S. side marsh, Interface layer	3 cm sub	85-03-24	250
15	Ile Grande	S. side marsh, SHWM, -1.5M	0-5 cm compo	85-03-24	320
16	Ile Grande	S. side marsh, SHWM, -1.0M	0-2 cm	85-03-24	7700
17	Ile Grande	S. side marsh, SHWM, -1.0M	0-2 cm	85-03-24	
18	Ile Grande	S. side marsh, SHWM	0-2 cm	85-03-24	7100
19	Ile Grande	S. side marsh, SHWM	Surface	85-03-24	
20	Ile Grande	S. side marsh, SHWM	Surface	85-03-24	8100
21	Ile Grande	S. side marsh, feeder channel	0-6 cm compo	85-03-24	
22	Ile Grande	S. side marsh, feeder channel	0-6 cm compo	85-03-24	
23	Ile Grande	N. side marsh #	0-1 cm	85-03-24	
24	Ile Grande	N. side marsh	0-0.25 cm	85-03-24	160
25	Ile Grande	N. side marsh	5-10 cm	85-03-24	11400
26	Ile Grande	N. side marsh	0-2 cm	85-03-24	520
27	Ile Grande	N. side marsh	2-5 cm	85-03-24	3100
28	Ile Grande	N. side marsh	5-10 cm	85-03-24	6500
29	Ile Grande	N. side marsh #	1-3 cm	85-03-24	6600
30	(No sample)				
31	Ile Grande	N. side marsh #	3-8 cm	85-03-24	300
32	Pointe de Toul	-a-Stain (?)	Surface	85-03-24	
33	Ile Grande	West of harbour -TOENOT	?	85-03-24	6400
34	Ile Grande	West of harbour -TOENOT	?	85-03-24	
35	Ile Grande	West of harbour -TOENOT	?	85-03-24	5300
36	Ile Grande	West of harbour -TOENOT	?	85-03-24	4900

16. DISCUSSION

The total hydrocarbon data shows significant levels of oil equivelants in all samples.

The large UCM's and hopane clusters indicate a high degree of weathering in the GC samples. Two samples (No. 10 and No. 22) differ from the majority only in the degree of weathering. Sample No. 10 is less weathered than most and sample No. 22 is less weathered than Sample No. 10.

IR data for sample No. 12 indicates a relatively low oil concentration (120 mg/kg). The alkane fine structure is probably of biogenic origin and has been mixed with a small amount of highly weathered oil.

Sample No. 34 does not appear to be from the Amoco Cadiz spill. If it was only a slightly weathered crude oil one would expect to find large isoprenoids. There are none present. The absence of a UCM would also indicate that this is not a weathered crude oil but rather a refined oil product.

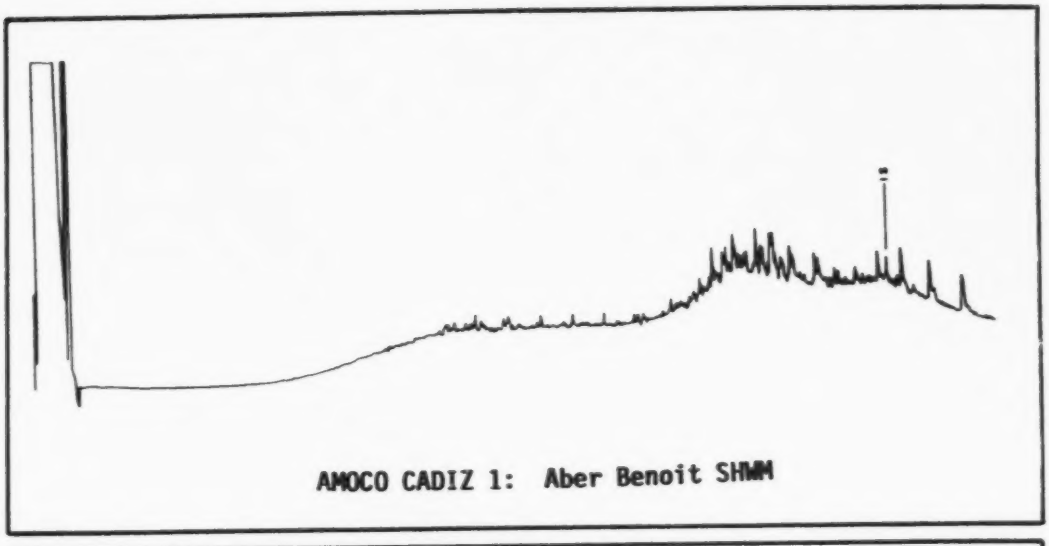
These results indicate that the weathering processes in the oil spilled in a temperate climate has progressed much further then the arctic stranded oil. There are two factors involved in the difference. The Amoco Cadiz oil was stranded in the spring of 1978. By the time the samples were collected, they had survived what may be considered as 84 open-water months. By contrast, the BIOS samples have survived at most 12 open water months. The temperatures to which the stranded oils have been subjected are very different. The highest temperatures at the Cape Hatt site are similar to the lowest temperatures at the Amoco Cadiz site.

For these reasons, any compositional similarities between the asphalt forming stranded oils are not apparent.

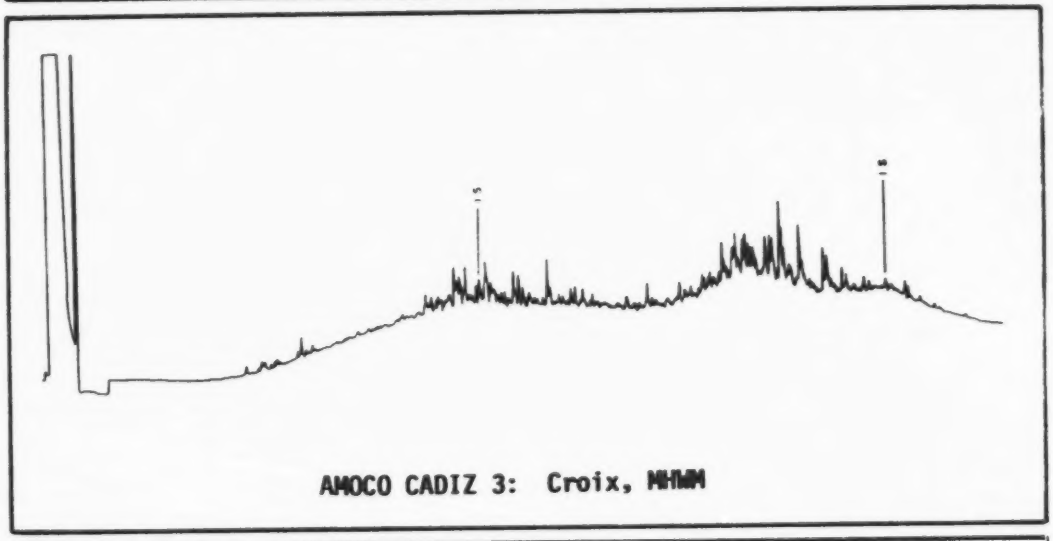
17. REFERENCES

Owens, E.H., and W. Robson. 1985. The Amoco Cadiz Incident. Site visits seven years after the spill. Report to Environment Canada, EE-63, Ottawa.

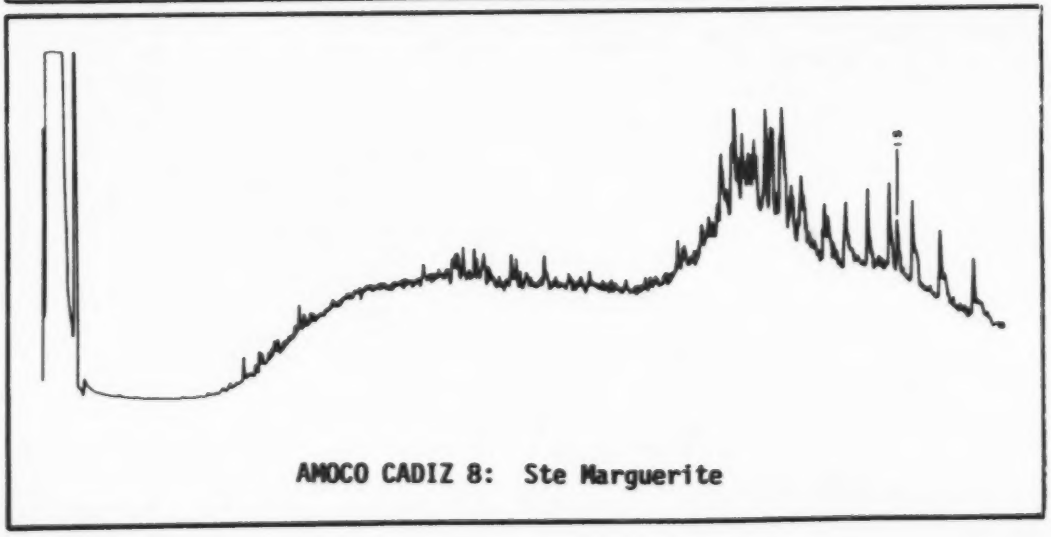
APPENDIX E: GAS CHROMATOGRAPHY



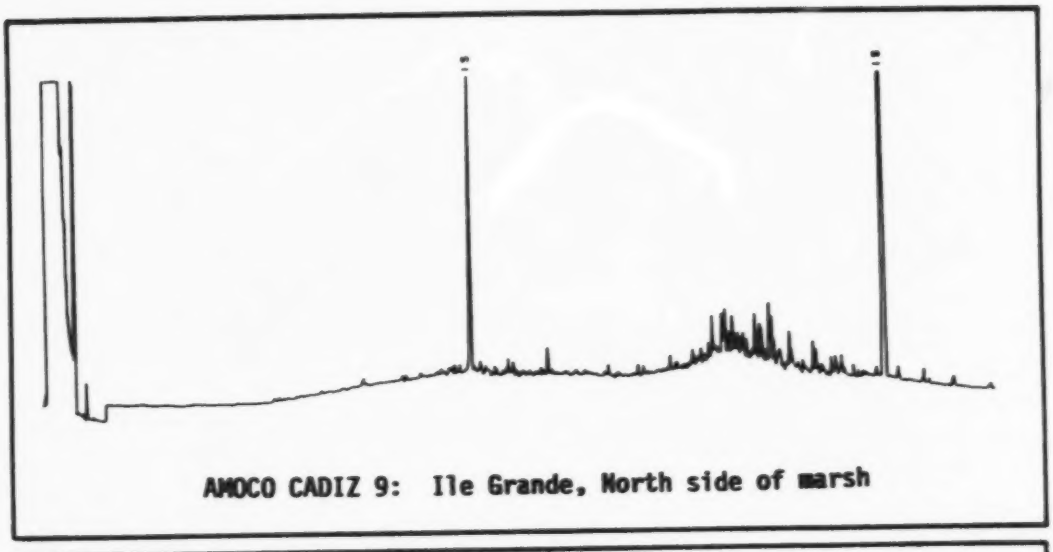
AMOCO CADIZ 1: Aber Benoit SHMM



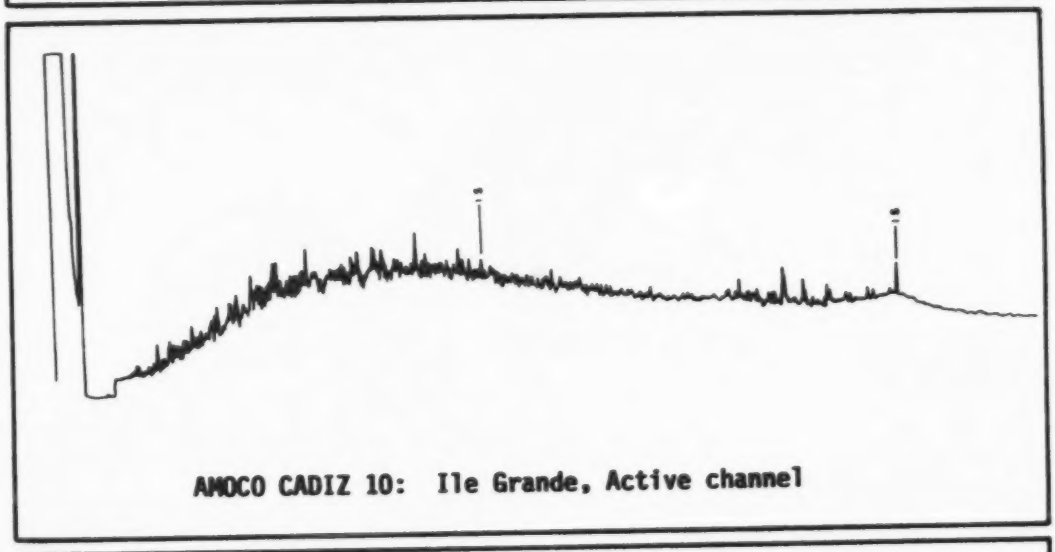
AMOCO CADIZ 3: Croix, MHMM



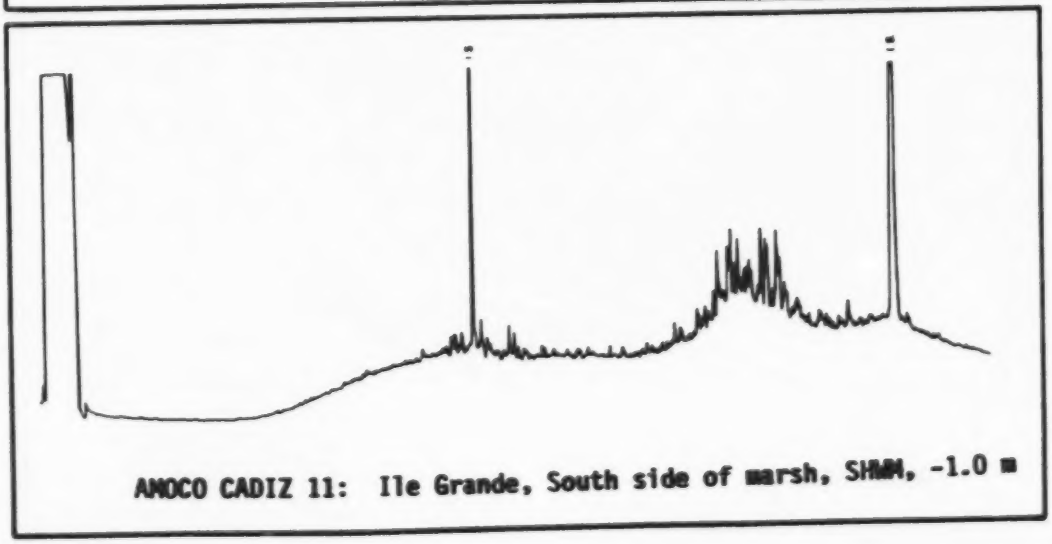
AMOCO CADIZ 8: Ste Marguerite



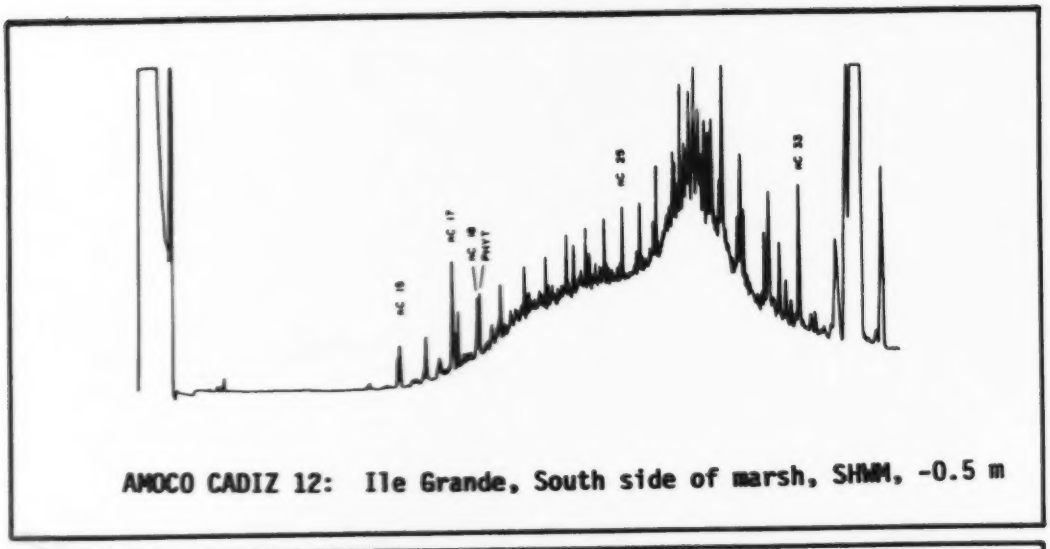
AMOCO CADIZ 9: Ile Grande, North side of marsh



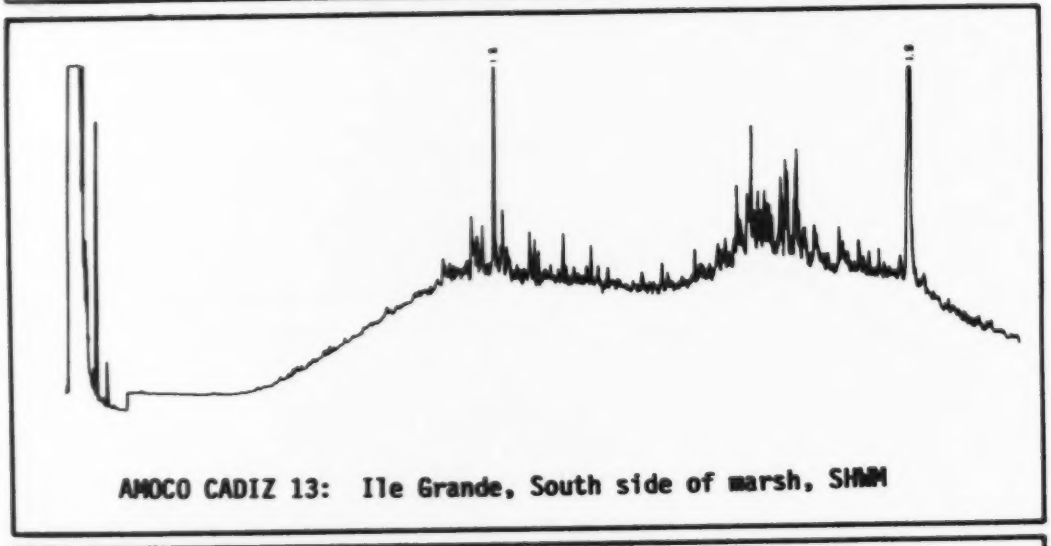
AMOCO CADIZ 10: Ile Grande, Active channel



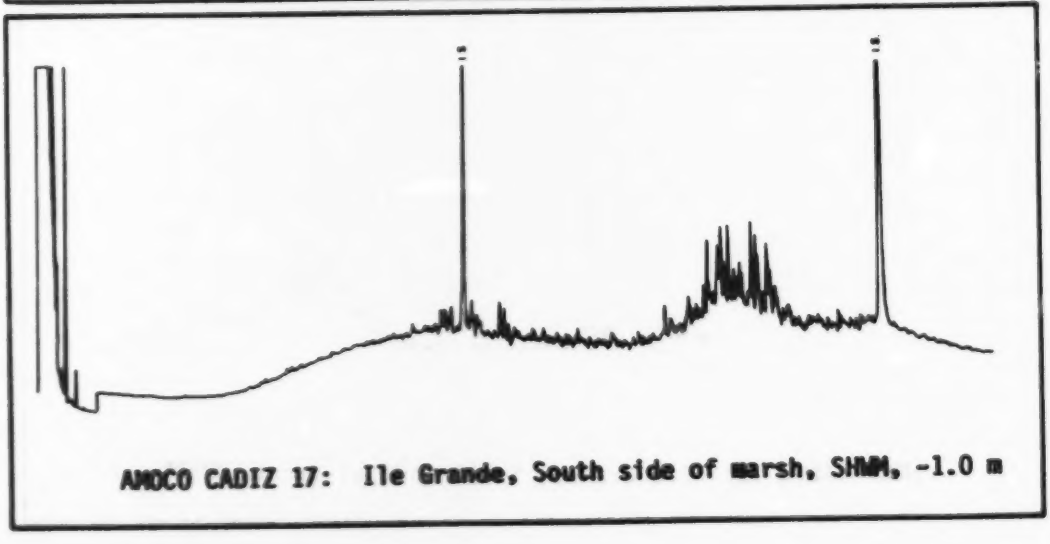
AMOCO CADIZ 11: Ile Grande, South side of marsh, SHWM, -1.0 m



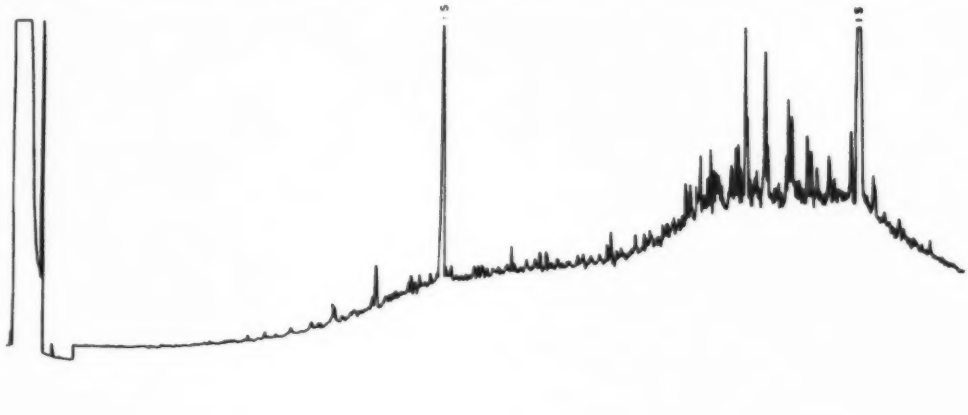
AMOCO CADIZ 12: Ile Grande, South side of marsh, SHMM, -0.5 m



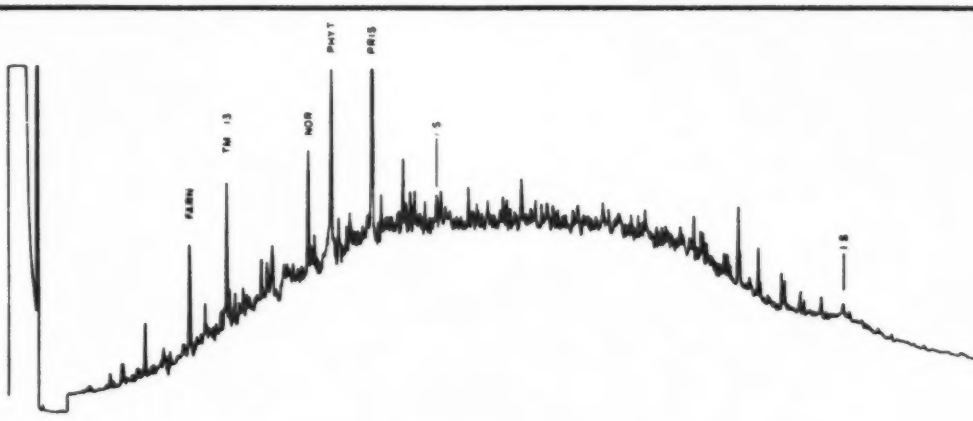
AMOCO CADIZ 13: Ile Grande, South side of marsh, SHMM



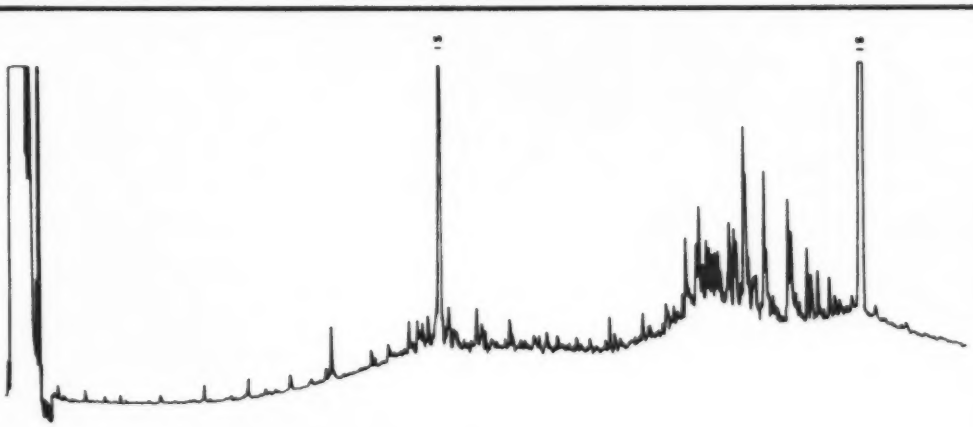
AMOCO CADIZ 17: Ile Grande, South side of marsh, SHMM, -1.0 m



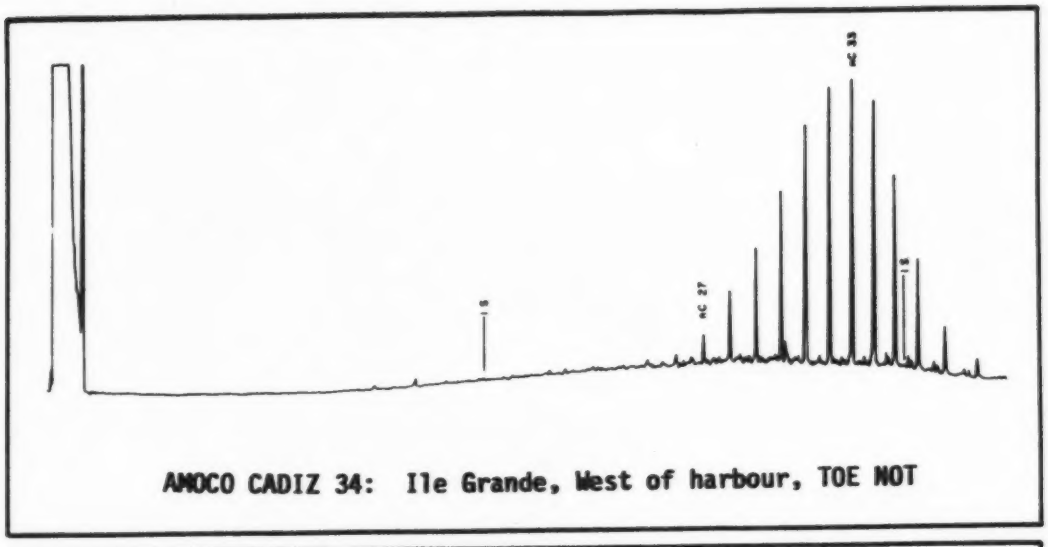
AMOCO CADIZ 19: Ile Grande, South side of marsh, SHMM



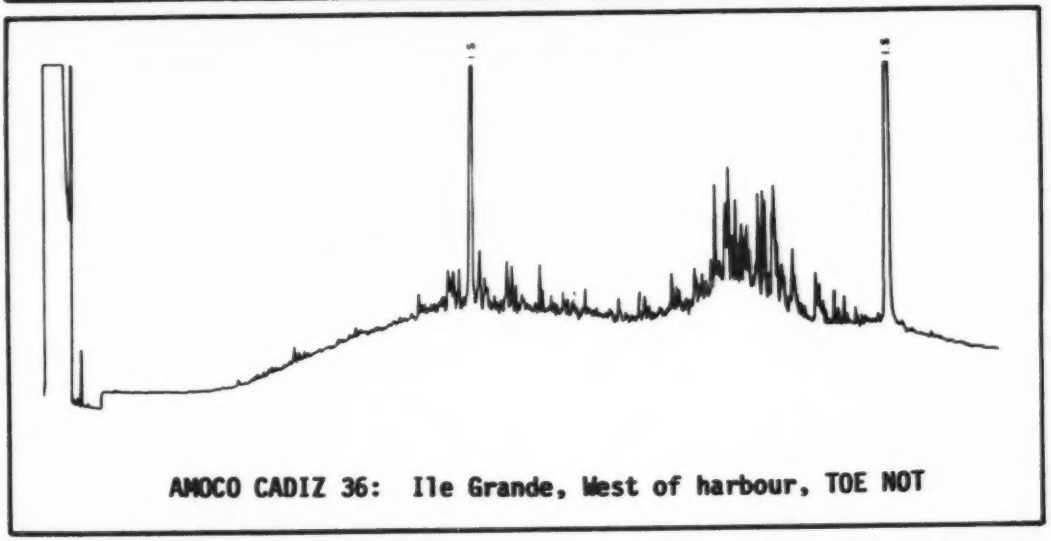
AMOCO CADIZ 22: Ile Grande, South side of marsh, feeder channel



AMOCO CADIZ 23: Ile Grande, North side of marsh



AMOCO CADIZ 34: Ile Grande, West of harbour, TOE NOT



AMOCO CADIZ 36: Ile Grande, West of harbour, TOE NOT